

University of Alberta

Removal of nitrogen compounds from bitumen-derived gas oil and its
impact on hydrotreating

by

Lina Del Rocio Parra Galvis

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©Lina Del Rocio Parra Galvis

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ABSTRACT

Nitrogen compounds present in bitumen and petroleum products cause significant inhibitory effects on processes such as catalytic cracking and hydrotreating due to poisoning of the catalyst. Consequently, selective removal of the nitrogen species may improve the efficiency of the above processes. Extraction of nitrogen compounds by complexation with copper chloride was found to be an efficient alternative; removal of all of the basic nitrogen and approximately 60% of the total nitrogen was accomplished. The novel invention in this study was the addition of liquid water which considerably improved both the rate of removal and the extent of removal, with no effect on the sulfur content.

Hydrotreating of the reduced-nitrogen extracts showed that the rate of sulfur removal was increased by a factor of 2.5 using a standard catalyst. Therefore, selective removal of nitrogen compounds would allow the use of smaller hydrotreaters and less severe operation conditions.

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CHAPTER 1:

Introduction and background

1.1 Introduction

The nitrogen compounds present in hydrocarbon streams have been an important research topic in the petroleum industry for a long time. Since the 1950's, studies attempted to explain the nature¹⁻³ and composition^{4, 5} of these compounds in petroleum streams. Previous studies have reported separation and identification schemes^{1, 5-7}. Thanks to this extensive research, nitrogen compounds present in petroleum are divided into two general types; basic compounds such as quinoline, pyridine, and their alkyl substituted derivatives; and non-basic compounds such as, indole, pyrrole, carbazole, and their alkyl substituted derivatives.

The existence of nitrogen compounds in hydrocarbon streams has led to increasing concern because of some major adverse consequences. These components cause poisoning of catalyst in acid catalyzed processes in the downstream, such as catalytic cracking⁸ and hydrotreatment (HDT)^{9, 10}. Nitrogen compounds are also found to be responsible to some extent for the low stability and degradation of fuels during storage, and some studies also revealed that nitrogen compounds contribute to a certain degree to gum formation during fuels storage¹¹.

In recent years, the quality of traditional crude has been diminished. Synthetic oil and heavier feed materials, with greater quantities of contaminants such as sulfur and nitrogen, have to be processed and refined to get better quality transportation fuels.

Recent environmental regulations have also become stricter¹² and are aimed to decrease the content of sulfur in transportation fuels to levels below 15 ppm. Previous research has determined that nitrogen compounds present in hydrocarbon streams strongly inhibit the hydrodesulfurization (HDS) process^{10, 13-15} increasing the required severity of the operating conditions. Studies have attempted to assess the reactivity of compounds such as carbazole and quinoline on HDS of diesel⁷. Pretreatment to remove nitrogen compounds prior to hydrotreatment of oil samples has shown an enhancement of the sulfur removal efficiency^{9, 16}. In this way, removal of significant quantities of nitrogen compounds from the hydrocarbon streams may enable more efficient sulfur removal processes. The challenge then is to find a suitable, efficient and economical pretreatment method for removal of nitrogen species from oil samples.

Various alternatives for removal of nitrogen compounds from petroleum, petroleum derivatives and synthetic crude oils have been investigated over the last 30 years. The efforts have been mainly focused on techniques such as adsorption¹⁷⁻²¹, complexation with metallic salts^{9, 16, 22}, extraction using conventional solvents^{23, 24} and ionic liquids²⁵⁻²⁸; Oxidation^{29, 30} and bidenitrogenation^{31, 32} have also been explored. In spite of all the efforts, every alternative has certain advantages and disadvantages over the others and none are yet used commercially. The type of feed material and the concentration of contaminants have to be considered when choosing one technique over the others. Furthermore, the efficiency of the removal process, the costs associated and the ease of the materials recovery have to be accounted for practical applications.

1.2 Objectives and Hypotheses

After a careful review of the literature, which is summarized in the following section, we selected the use of metal salts as the primary focus for the experimental work. The objective and hypotheses were then established:

Objectives:

- Determine the optimum experimental conditions for removal of nitrogen compounds by complexation with copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$). Except when specified otherwise, all references to copper chloride throughout the document indicate the dihydrate.

- Establish a procedure for recovery of the copper chloride particles after reaction.
- Assess the impact of nitrogen removal on hydrotreating (sulfur removal) of the gas oil samples.
- Verify the suitability of nitrogen complexes as feed material for gasification experiments.

The aim of this study is to prove if the following hypotheses are valid:

- Significant removal of nitrogen compounds from a high nitrogen-containing gas oil feed can be accomplished by complexation with copper chloride.
- Reduction of the nitrogen content of the feed material has a positive impact on the hydrotreatment of the sample by increasing the sulfur removal efficiency under the same reaction conditions.

1.3 Background

1.3.1 Nitrogen compounds

Nitrogen compounds are found in petroleum sources in different quantities and distribution; in general, there are two types of nitrogen compounds: basic and non-basic. Quinoline, pyridine, acridine and all their alkyl substituent derivatives are classified as basic compounds due to the unshared pair of electrons present on their structures; shown in Table 1-1. Indole, carbazole and all their alkyl substituent derivatives are classified among the non-basic type; some of their structures are shown in Table 1-2. For every ring structure illustrated in these tables, the predominant compounds present in actual petroleum fractions would be substituted by a wide variety of alkyl and cycloalkyl groups, such as the illustrated example of 1,2,3,4-tetrahydrocarbazole.

The lone pair of electrons present on basic nitrogen compounds (Lewis bases) allows them to react with electron pair acceptors (Lewis acids) to form complex compounds. This characteristic is of special importance on acid catalyzed processes where the active sites on the catalyst surface can be competitively occluded by the basic nitrogen compounds in the feed. Researchers found that the contact of the catalyst with nitrogen compounds blocks the interaction of the catalyst with the sulfur compounds in the feed, reducing their reaction and removal^{33, 34}

Table 1-1 Structure of basic nitrogen compounds

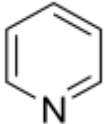
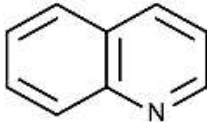
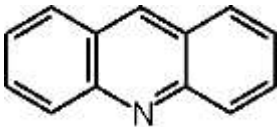
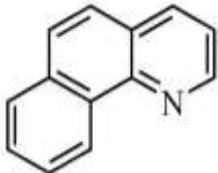
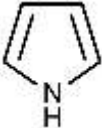
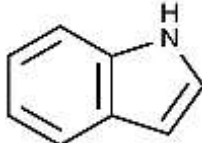
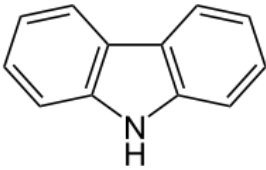
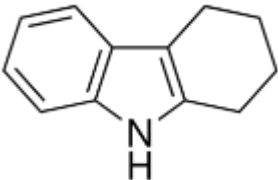
Compound	Structure
Pyridine	
Quinoline/ benzopyridine	
Acridine	
7,8-Benzoquinoline	

Table 1-2 Structures of non-basic Nitrogen compounds

Compound	Structure
Pyrrole	
Indole	
Carbazole	
1,2,3,4-Tetrahydrocarbazole	

Zeuthen et al.³⁵ found that nitrogen compounds have lower reactivity than the corresponding sulfur compounds in hydrotreatment. From their experiments they determined that even 97.7% of the highly refractory sulfur-compound 4,6-dimethyldibenzothiophene (DMTB) was converted during HDT; on the other hand, only approximately 77% of the nitrogen compounds were converted in the process.

Other studies have appreciably enhanced our knowledge about nitrogen species in different oil sources and their impact on HDT^{36, 37}. Shin et al.⁷ studied the composition of nitrogen compounds in three different gas oil samples. The results showed similar distributions of the species but different relative abundance. Hydrotreatment experiments on the oil samples were attempted to determine the reactivity order of nitrogen species. It was determined that the reactivity is influenced by the number and the position of substituted methyl groups. In general, as the number of methyl groups increased, the reactivity of nitrogen species decreased⁷. Sumbogo et al.³⁶ used gas oil and its nitrogen species-free oil samples on their hydrotreatment experiments with different types of catalysts. The experimental set up included a series of runs having a second stage that was operated by renewal of the H₂ in reaction atmosphere. This second stage was intended to avoid inhibition caused by accumulation of H₂S. They compared the concentration of specific sulfur species in the oil samples after hydrotreatment with and without pretreatment for nitrogen removal. It was found that the inhibition extent varies according to various factors including the type of catalyst, the acidic nature of the catalyst and the concentration of the nitrogen species.

In general, reduction of the nitrogen levels in high nitrogen-containing feed streams by hydrotreatment demands more severe conditions with large hydrogen consumption due to the competitive adsorption of nitrogen and sulfur compounds for the active sites on the catalyst surface^{34, 38, 39}. The greater hydrogen consumption and the more severe process conditions directly impact the operating costs of the HDT process.

1.3.2 Nitrogen and sulfur content in petroleum and bitumen derived fractions

The average nitrogen and sulfur content in conventional crude oils is approximately 0.1 wt% and 0.8-1% respectively⁴⁰. In synthetic crude oils derived from shale oils and oil sands, the nitrogen content is much higher, approximately 0.5 to 2.5 wt%¹⁵. The typical content of nitrogen and sulfur of some synthetic crude oils (SCO) are shown in Table 1-3. Table 1-4 shows a typical analysis from various SCO, and content of contaminants.

Table 1-3 Nitrogen and sulfur content of various synthetic crude Oils³⁸.

Nitrogen content of gas oils from oil sands	(ppm)	MW	mol % N compounds
Syncrude coker heavy gas oil	2900	380	7.90
Syncrude light gas oil	1443	290	3.00
Shell heavy vgo (454-565C)	4046	380	11.0
Shell light VGO (343-454 C)	2125	290	4.40
Sulfur content of gas oils from oil sands	(wt%)	MW	mol % S compounds
Syncrude coker heavy gas oil	3.57	380	42.4
Syncrude light gas oil	1.70	290	15.4
Shell heavy VGO (454-565C)	2.20	380	26.1
Shell light VGO (343-454 C)	1.90	290	17.2

Table 1-4 Typical analysis from various SCOs and a conventional crude blend¹⁵.

*Vacuum Gas oil from Rainbow/Zama crude oil.

** Vacuum Gas oil from bitumen derived oil

*** Deasphalted Oil from bitumen derived oil

Feed name	Rainbow /Zama crude VGO*	Untreated Coker VGO**	Untreated LC-finer VGO**	Untreated virgin VGO**	DAO from bitumen***
Cut range, C	343-524	343+	343-524	343-524	As received
Density at 15C	0.8988	1.004	0.9562	0.9712	0.9776
API gravity, API	25.9	9.4	16.5	14.2	13.2
Sulfur, ppmw	9170	40100	13500	32500	35400
Total Nitrogen, ppmw	800	4010	3370	1930	3050
Basic nitrogen, ppm (wt)	240	1212	991	610	815
Carbon, wt%	86.34	85.09	87.03	85.09	84.72

Microcarbon residue, wt%	0.08	2.86	0.24	0.33	5.37
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1.3.3 Copper chloride

Copper (II) chloride is one of the most common copper (II) compounds. Copper (II) chloride (CuCl_2) is a transition metallic salt, light brown solid, highly hygroscopic which slowly absorbs moisture to form a dihydrate compound. CuCl_2 is ionic, highly soluble in water and it chemically behaves as a Lewis acid.

Most copper (II) compounds exhibit distortions from an idealized octahedral structure due to the Jahn-Teller effect which is most often encountered in octahedral complexes of the transition metals^{41, 42}. The Jahn-Teller effect describes the localisation of one d-electron into a molecular orbital explicitly strongly antibonding with respect to a duet of ligands⁴¹. In the structure of $\text{CuCl}_2(\text{H}_2\text{O})_2$, the Cu(II) center is surrounded by two water ligands and two chloride ligands, which bridge asymmetrically to other Cu centers.

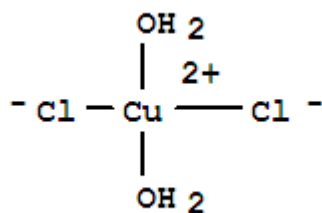
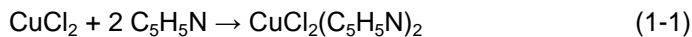


Figure 1-1 Structure of copper chloride dihydrate

Copper (II) chloride reacts with a large variety of ligands such as pyridine or triphenylphosphine oxide to form coordination complexes as shown in equations 1-1 and 1-2 below:



1.3.4 Process technology for removal of nitrogen compounds

1.3.4.1 Hydrotreatment

Hydrotreatment (HDT) is applied extensively in petroleum refining to remove heteroatoms from the feed for further processing or to meet product specifications. HDT includes simultaneous hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions, as well as hydrodeoxygenation (HDO), hydrodearomatization (HDA), hydrodemetallization (HDM), hydrogenation of olefins, and hydrogenation of aromatics.

Figure 1-1 shows the schematic of a conventional hydrotreating process for diesel.

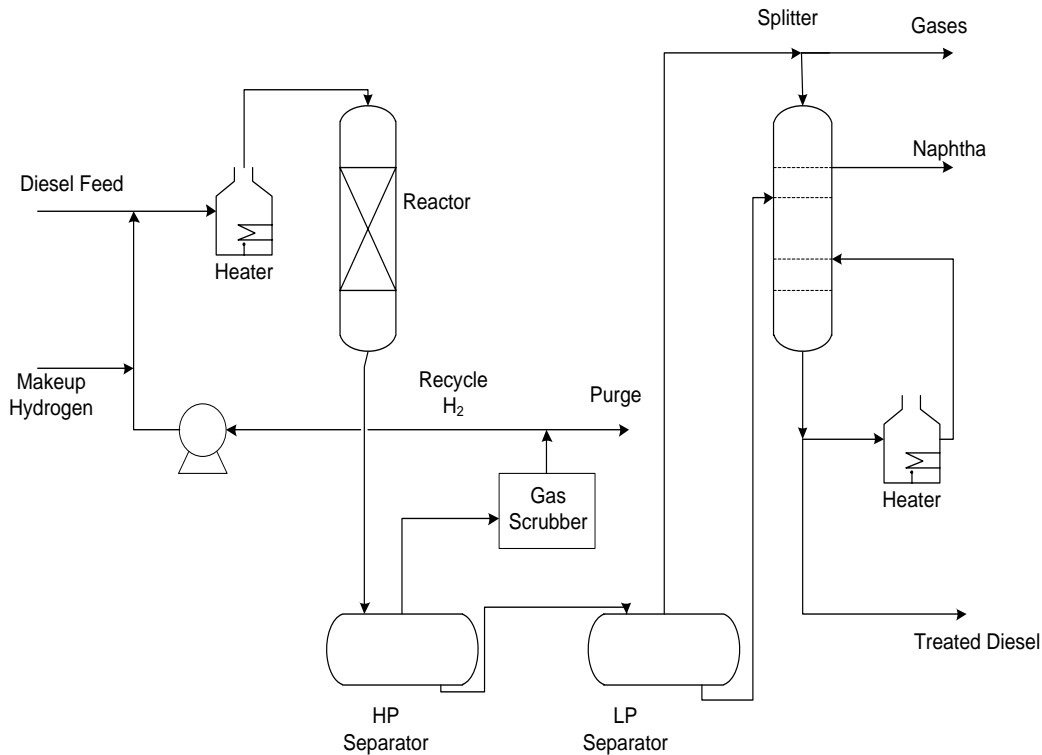


Figure 1-2 Schematic of a diesel hydrotreating unit³⁹

In general, HDN is the most difficult reaction during hydrotreatment^{34, 43}. More research is needed to determine which nitrogen compounds are the most problematic and what are their mechanisms of conversion and kinetics during HDN processes.

Hydrodesulfurization in principle follows a direct S-C cleavage^{38, 43}. In HDS, the breaking of the C-S bond can be achieved by two observed mechanisms^{34, 38}. One is by direct

elimination of the sulfur atom in a single step to form H₂S and an alkene or by hydrogenation of the aromatic ring preceding the attack to the sulfur atom. In the second mechanism, C–S bonds are broken and C–H and S–H bonds formed at the same time³⁴. On the other hand, HDN proceeds through a hydrogenation pathway. Nelson and Levy³⁴ indicated that direct C–N cleavage is not possible in heterocyclic aromatic molecules; so, hydrogenation is the dominant pathway in HDN. Once the aromaticity of the molecule is eliminated, C–N bonds become aliphatic and C–N bond breaking becomes feasible; complete hydrogenation of the aromatic ring is necessary before N–C cleavage, so HDN requires much larger hydrogen consumption than HDS.

In general, HDN has not been studied as intensively as HDS. In the past, the nitrogen content in petroleum fractions was lower than in streams derived from bitumen and heavy oil; which have been increasing as predominant feed to refineries. The impact of the presence of nitrogen compounds in the feed is more significant under the existing conditions.

Table 1-5 Operating parameters for hydrotreating different feedstocks⁴⁴

Operating Parameter	Naphtha	Kerosene	Gas Oil	Vacuum gas oil	Residue
Boiling range (°C)	70-180	160-240	230-350	350-550	>550
Operating Temperature (°C)	260-300	300-340	320-350	360-380	360-380
Hydrogen pressure (bar)	5-10	10-30	15-40	40-70	120-160
Hydrogen consumption (wt%)	0.05-0.1	0.1-0.2	0.3-0.5	0.4-0.7	1.5-2.0
LHSV* (h ⁻¹)	4-10	4-4	1-3	1-2	0.15-0.3

*LHSV, Liquid volumetric flow rate at 15°C (ft³/h)/volume of catalyst (ft³)

1.3.5 Alternative technologies for removal of nitrogen compounds

The search for pre-treatment methods which allow removal of significant quantities of nitrogen compounds from different feed materials has been one of the main challenges in the refining industry. Hydrotreatment has been the only technology industrially applied for removal of nitrogen species. The use of heavier feed materials, with higher nitrogen content has led to an increase in the severity of the operating conditions and higher hydrogen consumption (Table 1.5)

The predominant factors that were considered in order to decide on a potential alternative for experimental work in this project were: efficiency of nitrogen removal, selectivity of nitrogen over other compounds, amount of material required for the process, and regeneration. More specifically, it was critical to evaluate the capability of every technique for dealing with high nitrogen, sulfur and aromatics content of the feed streams of interest.

Several alternative methods to HDT have been reported in the last two decades. One of the most explored methods for removal of nitrogen compounds from a wide variety of feed materials has been adsorption onto different kinds of high-surface area solids. Research in this field demonstrated that adsorption is essentially effective for low nitrogen content feeds. Complexation using transition metallic salts showed better performance with high nitrogen content feeds. Extraction with ionic liquids has also been proposed as an alternative to replace conventional solvents. Xie et al.^{26, 28} and Serban et al.²⁵ showed some interesting results when using low and high content nitrogen feeds.

1.3.5.1 Adsorption

Adsorption is the adhesion of one or more components from a gas or liquid stream onto a solid surface⁴⁵. Molecules are added to the surface due to the existence of non-compensated attractive forces on the adsorbent surface. The forces involved in the physical adsorption include van der Waals (repulsion and dispersion) and electrostatic interactions⁴⁶.

Removal of nitrogen compounds from liquid streams using adsorption has been one of the most investigated approaches over the past decades in the petroleum industry, both for analytical and preparative separations in the laboratory, and for industrial scale use. Several types of materials have been reported as adsorbents⁴⁷ in denitrogenation of different feed materials. Some examples to be mentioned are silica or silica–alumina⁴⁸, activated carbons^{20, 21}, oxalic acid⁴⁹, and shale ash¹⁸. Furthermore, a Korean company reported, patented and tested an adsorption process that removes circa 90% of the nitrogen compounds from diesel fuel streams using silica gel as an adsorbent^{19, 48}.

The general procedure consists of contacting the feed material with a selected adsorbent at predetermined conditions in a vessel with mixing. The mixture is left in contact for enough time for the adsorption process to take place. In the continuous flow phase, the

velocity and residence time are controlled to ensure efficient adsorption. The denitrogenated oil is subsequently separated from the mixture by simple decantation or by filtration. The final product oil is analyzed for nitrogen content. The adsorbent is then either regenerated to be reused in the process or discarded in the case of analytical preparations.

When the viscosity of the feed material is too high, as in the case of shale oil, a pretreatment including heating or dissolution with a solvent may be required to obtain adequate mixing, contacting and separation of the adsorbent¹⁸. The type of vessel used varies according to the purpose and feed material used. Sano et al.^{20, 21} used a stainless steel tube packed with the selected adsorbent and the oil feed was pumped through the bed. Almarri et al.¹⁷ used a stirred batch system (a capped tube and electromagnetic stirring system); there is not a standard vessel for adsorption processes, although in industrial scale operations, packed beds are the norm unless frequent replacement of the adsorbent is required.

Crude and synthetic crude oil streams typically contain nitrogen and sulfur compounds with a large amount of structurally similar aromatic compounds^{38, 50}, consequently, one of the main challenges is to find an adsorbent that selectively adsorbs the nitrogen compounds, leaving unaffected the content of the coexisting compounds present in the feed.

In their experimental work, Sano et al.^{20, 21} removed sulfur and nitrogen species from straight run gas oil (SRGO) by adsorption over activated carbon. Oxidants such as HNO₃, H₂SO₄ at room temperature were used in the activation process. They examined in detail a particular activated carbon of very large surface area, MAXSORB-II, which showed better results than the other activated carbons throughout the process. They also found that as they increased the amount of oil feed treated in their experiments, the percentage of nitrogen compounds removed decreased.

Min et al.^{19, 48} developed a pretreatment adsorption process to remove nitrogen compounds from diesel fuel using silica gel as adsorbent. The nitrogen content range of the oil feed was 179-720 ppmw. The level of nitrogen removal was found to depend on the oil feed and nitrogen content; nitrogen removal achieved was in the range of 70-86%. They also evaluated the effects of the denitrogenation pretreatment on the hydrodesulfurization of the treated oil under conventional conditions to assess the

improvement on the HDS process. The major benefit that was identified from the denitrogenation pretreatment was in terms of the degree of reduction in temperature. If the denitrogenated oil was fed instead of the untreated oil, the temperature required to get the same sulfur removal under the same conditions dropped by 20 °C.

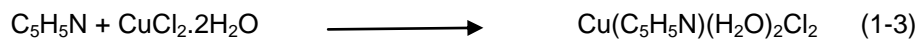
This method was also patented⁴⁸, and in the patent document they discuss in more detail the procedure and adsorbents employed in their experiments. Different oil feeds with various nitrogen contents (156- 2503 ppmw) were used. As the nitrogen content in the feed increases, the percentage of nitrogen removal is substantially decreased. With the proposed adsorbent and process configuration, this technique is adequate for low nitrogen content feed but it is not likely to work well for high nitrogen content feeds.

The effects of the adsorption temperature, reaction time, ratio of adsorbent to feed, characteristics of the adsorbent (surface area, oxygen content) and regeneration of the adsorbent are some of the variables investigated throughout the literature. The main limitations of this process are the large mass of adsorbent required, the simultaneous adsorption of aromatics and sulfur compounds and the regeneration of the adsorbent. In general this method is most suitable for analytical lab-scale preparation and removal of trace contaminants.

1.3.5.2 Complexation with metallic salts

In complexation reactions, a chemical reaction occurs between a metal ion and a ligand that contains at least one atom with an unshared pair of electrons. The product is a complex molecule or coordination compound linked through a coordinate covalent bond, both of the bonding electrons are provided by the ligand⁵¹. In these kinds of complexes the central atom acts as an electron-pair acceptor (Lewis acid) and the ligand as an electron-pair donor (Lewis base).

An elementary complexation reaction between pyridine and copper chloride is shown in equation 1-3 below:



Crystalline transition metal salts^{9, 16, 22} have been investigated as complexing agents for nitrogen removal. Choi and Dines^{16, 22} tested various transition metal salts; they observed that copper (II) chloride salts presented the highest nitrogen removal values among the examined salts. Copper (II) chloride salts with different hydration number were

also tested. It was determined that $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was the most effective compound in forming complexes with a wide variety of nitrogen compounds. Narangerel and Sugimoto⁹ also reported high nitrogen removal efficiency using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ for complexation reactions with high nitrogen content feeds.

The reason for the superior performance of copper chloride salts in complexation reactions with nitrogen compounds is not well understood. The nitrogen atom in aromatic nitrogen compounds such as pyridine can easily form complexes with transition metal salts by donating the electron pair to acidic metal cations such as Zn^{2+} or Cu^{2+} . The metal-N bond so formed neutralizes the acidic character of the cations.

The debate on the preference of certain metal ions to form complex ions with determined ligands has been widely discussed in the chemical literature for many years. One of the most accepted theories is the hard-soft acid/base (HSAB) principle proposed by Pearson at the beginning of the 1960s. The general rule of thumb is that hard Lewis acids tend to combine with hard Lewis bases, and soft acids with soft bases. The closer on the Periodic Table that a metal ion is to gold, the softest element, the softer that metal ion is; and the farther from gold, the harder the metal cation⁵¹.

Pyridine is classified as a borderline base according to the HSAB principle. There are additional properties of ligands beyond their HSAB characteristics that determine their bonding preferences to metal ions. Choi and Dines²² concluded that the capacity of some transition metal salts to form complexes with pyridine was also affected by various factors including the Lewis acidity of the metal as well as structural factors of the salts.

Narangerel and Sugimoto⁹ used copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) to remove nitrogen compounds from various synthetic crude oils (SCOs). Light gas oil derived from shale oil with 0.5-2.5 %wt. of N compounds, coal-derived liquids, and pyrolysis product of Athabasca bitumen were the feed materials for their experiments. In their study, they varied the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to oil feed weight ratio for each SCO. Their results showed acceptable nitrogen removal (50-88% depending on the feed material) for high nitrogen content feeds with low salt to oil feed weight ratios required. The oil recovery of the process, when bitumen was treated, was very high at around 97%. For shale oil and coal liquids, the oil recovery was not as high as in the case of bitumen, probably due to the different composition of these streams. The maximum decrease in nitrogen content for the synthetic liquids tested were from 9900 to 1780 ppmw in shale oils, from 4500 to 700 ppmw in coal liquids and from 1260 to 480 ppmw in bitumen-derived light gas oil. The

results of this study also suggest a high selectivity for nitrogen compounds during the removal process. Basic and non-basic compounds were removed, with preferential removal of basic compounds. It was found that the re-using the copper salt did not affect the complex-forming potential.

These previous research efforts identified complexation as a promising alternative for removal of nitrogen species from bitumen-derived streams. More studies are required in order to verify its real potential. The following factors are critical for the complexation process in order to evaluate its potential: high percentage of nitrogen removal, small amounts of complexing material required to carry out the separation, selectivity and regeneration of the complexing material

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1.3.5.3 Extraction with ionic liquids

Ionic liquids (ILs) are low-temperature molten organic salts, in some cases with melting points below room temperature. They have some useful properties such as very low vapour pressure (low volatility), low flammability, wide liquid range, solvating properties^{52, 53} for a variety of compounds and high thermal stability (which is sometimes overstated). Commonly, ionic liquids have higher density than organic liquids and water⁵⁴. Another property of ionic liquids is their miscibility with water and organic solvents, which can be altered by adjusting the side-chain length on the cation and by the choice of the anion⁵³. In addition, ionic liquids can act as acids or bases⁵³. All the attractive characteristics mentioned above have brought attention to ionic liquids as an alternative to replace volatile organic solvents in organic chemistry and engineering^{53, 54}. Some of the properties of a few common ionic liquids are shown in Table 1-6, along with the abbreviation commonly used.

Table 1-6 Ionic liquids names and properties^{52, 54}

Full name	Short Name	Density at 80 °C g/cm ³	Molar mass
1-Ethyl-3-methylimidazolium ethyl sulfate	[EMIM]EtSO ₄	1.24	236.29
1-Butyl-3-methyl imidazolium hexafluorophosphate	[BMIM]PF ₆	1.38 g/mL at 20 °C	284.18
1-Butyl-3-methyl imidazolium tetra fluoroborate	[BMIM]BF ₄	1.15	226.02
1-Butyl-3-methylimidazolium chloride	[BMIM]Cl	1.0528	174.67
1-Butyl-3-methylimidazolium hydrogen sulphate	[BMIM]HSO ₄	---	236.29
1-Butyl-3-methylimidazolium methyl sulfate	[BMIM]CH ₃ SO ₄	1,21 (20 °C)	250.32
1-Butyl-3-methylimidazolium Octyl sulphate	[BMIM]Oc-SO ₄	---	348.50
1-Ethyl-3-methyl imidazolium tetra fluoroborate	[EMIM]BF ₄	1.23	197.97
1-n-Amyl-3-methyl-imidazolium hexafluorophosphate	[AMIM] PF ₆	----	---
1-n-Amyl-3-methyl-imidazolium tetrafluoroborate	[AMIM] BF ₄	----	-----

In the last decade, several studies regarding selective extraction and identification of nitrogen species using ionic liquids have been published²⁵⁻²⁸. Xie et al.^{27, 28} published a series of studies concerning separation and identification of nitrogen compounds using chloride based ionic liquids. One of the main objectives in the series of studies²⁷ was to assess the miscibility of 1-butyl-3-methyl-imidazolium chloride in a toluene/*n*-dodecane mixture. Extraction of dibenzothiophene, indole and pyridine from *n*-dodecane using 1-butyl-3-methyl-imidazolium chloride (BMIm⁺Cl⁻) was carried out with single component solutions containing 100 ppm of nitrogen in the form of neutral nitrogen compounds or 100 ppm of sulfur. BMIm⁺Cl⁻ was found to be slightly soluble in the hydrocarbon mixture under this conditions; when toluene is added to the model mixture, the extraction of a single component from the mixture by BMIm⁺Cl⁻ depends on the toluene/*n*-dodecane

ratio. The results of the study also showed preference of the ionic liquid for neutral nitrogen compounds and high selectivity for nitrogen over sulfur species.

Another approach has been the use of ionic liquids for simultaneous sulfur and nitrogen compounds removal processes. Zhang et al.⁵⁵ tested two types of ionic liquids for simultaneous sulfur and nitrogen removal from a model fuel as well as different types of transportation fuels. The first type of ionic liquid was 1-alkyl-3-methylimidazolium tetrafluoroborate (short-chain 1-alkyl and water miscible) and hexafluorophosphate (water immiscible) based ionic liquids. The second type was trimethyl-amine hydrochloride (AlCl₃-TMAC).

The absorption efficiencies of the first type of Ionic liquids were compared using two model fuels. It was found that 1-Butyl-3-methyl imidazolium tetra fluoroborate [BMIM]BF₄ was more selective for thiophene. Various model compounds were also studied to determine the applicability of the ionic liquids for nitrogen compounds removal. Pyridine and 2-methylpyridine were found to be completely miscible with [BMIM]BF₄ while piperidine and 2-methylpiperidine, showed limited absorption into the ionic liquid. The use of [BMIM]BF₄ with a model fuel constituted by a mixture of *n*-C12, dibenzothiophene (DBT), and either pyridine, or piperidine allowed simultaneous removal of sulfur and nitrogen species, but the absorption capacity was diminished in comparison to individual compounds.

According to the earlier study, regeneration of the ionic liquid and recovery of the absorbed compounds can be carried out by two different methods depending on the characteristics of the Ionic liquids (ILs). For water-miscible ILs such as [EMIM]BF₄, the absorbed compounds can be released by addition of water into a separated phase; aromatic sulfur compounds are quantitatively removed from the ionic liquids due to the stronger interaction of water molecules with the ionic liquid. Water can be subsequently vaporized from the ionic liquid. For water immiscible liquids, the IL regeneration can be accomplished by direct distillation. Nuclear Magnetic Resonance (NMR) analyses indicated that the ionic liquid preserved their original structures after the regeneration processes.

Serban et al.²⁵ tested various acidic compounds (pH<7) for removal of nitrogen compounds from a mixture of model compounds and from a variety of nitrogen-containing hydrocarbon streams. Straight Run Diesel (SRD), Light Cycle Oil (LCO) and Light Coker Gas Oil (LCGO), with nitrogen content ranging between 100 and 1716 ppmw

were used as feed material for the experiments. The AIL's tested were 1-ethyl-3-methylimidazolium ethylsulfate [EMIM]EtSO₄, 1-butyl-3-methylimidazolium hydrogen sulphate [BMIM]HSO₄ and 1-butyl-3-methylimidazolium methyl sulfate, [BMIM]CH₃SO₄.

The acid ionic liquids tested showed good performance during the extraction process and some desirable characteristics such as insolubility in the feed, low solubility for the nitrogen-free hydrocarbons, as well as ease of recovery. The extraction equilibrium was found to be reached in a very short time.

From their experimental work, 1-butyl-3-methylimidazolium hydrogen sulphate [BMIM]HSO₄ was established to be the AIL which produced the higher nitrogen removal efficiency when using it for extraction from Light Coker Gas Oil LCGO (1716 ppmw N). Up to 80% of the initial nitrogen content was removed with a 0.5 AIL to LCGO weight ratio. Gas chromatography analysis of the product showed high selectivity for nitrogen compounds with the sulfur content remaining almost unaffected during the process. After regeneration, the ionic liquid lost between 2.5 and 4.5% of its extraction capacity for total and basic nitrogen²⁵. As a final part of their study, they also performed some comparative hydrotreatment tests for the denitrogenated feed and the untreated oil samples to assess the improvement on the operating conditions during the HDT when nitrogen is reduced. The following are the most remarkable findings: the catalyst requirement for the untreated feed was about 50% more than for the denitrogenated feed; the required temperature to achieve the same level of sulfur removal for the denitrogenated feed was about 19°C lower compared to the untreated feed.

The large amounts of ionic liquids that have to be used in liquid-liquid extraction processes²⁵ were a concern for the researchers. The usage of ionic liquids instead of conventional solvents may also result in a much more expensive process alternative; so the exploration of further alternatives and research focused on the prospect of supported membranes using ILs for extraction of nitrogen species.

Matsumoto et al.⁵⁶ reported the use of supported membranes using Imidazolium- based ionic liquids; their study attempted to determine the permeability of nitrogen compounds from a model mixture through the membrane. The feed solutions were a mixture of organic nitrogen compounds: quinoline, isoquinoline, pyridine and *n*-heptane. Organic nitrogen compounds were found to selectively permeate the Supported Liquid Membrane (SLM). It was also found that the permeation rates of the compounds in this study were ten times higher than those of aromatic compounds (benzene, toluene and *p*-xylene), mainly due to the polarity differences. Permeation rates through SML based on

ILs were mainly controlled by the polarity of the permeating species but hydrophilicity of the species should be considered if polarities are similar⁵⁶.

The results of the studies mentioned above demonstrated the potential of ionic liquids as a process alternative for nitrogen removal. The main limitation in this process could be the higher cost of ionic liquids compared to conventional solvents. The high amount of material required is one of the concerns but, if regeneration of the ionic liquids can be successfully carried out and the solvent can be reused in the process, the cost won't be the deciding factor. Experimental work is necessary to determine the performance of specific ionic liquids for removal of nitrogen species from high content nitrogen feeds.

1.3.5.4 Oxidation of organic nitrogen compounds

The general procedure for removing nitrogen compounds from petroleum by oxidation is described in the U.S patent 3847800 by Guth et al.⁵⁷. It comprises contacting the feed oil with an oxidizing agent such as a gas mixture with one or more oxides of nitrogen or a liquid mixture such as hydrogen peroxide and acetic acid^{29, 58}. The organic compounds are oxidized into compounds that can be easily removed from the oil by a selective solvent.

Guth et al.⁵⁷ employed a gas mixture of oxides of nitrogen with two or more nitrogen atoms (e.g. NO₂, N₂O₃, N₂O₅) which was contacted with the feed. The product stream was subsequently mixed with methanol in which the oxidized sulfur and nitrogen compounds were soluble but the oil was immiscible. Separation of the two phases can be carried out by decantation or centrifugation due to the differences in their densities. The solvent recovery can be carried out by distillation to be reused in the process. The reaction time employed in their experimental work ranges between 2h and 20h.

One of the main constraints of this process is selectivity. Many compounds can react during the process and form undesired compounds such as coke and polymers which can be a problem for further refining; some compounds which are of great importance for the downstream processes such as olefins can also be oxidized^[13]. Pre-treatment of the feed was proposed. For example Guth et al.⁵⁷ suggested a pre-treatment step consisting of heating to 150-300°C for a period of time, which permits some reactive groups in the feed to combine with other hydrocarbon molecules and thus become less reactive.

Da Conceição et al.²⁹ investigated oxidants which selectively oxidize the organic nitrogen compounds present in the feed without affecting the other kinds of compounds. Sample volumes (50-150ml) were deposited in a vessel and the sample was heated to 70°C under agitation conditions. A mixture of ethanoic acid and hydrogen peroxide was added and the stirring continued for 1h, after that time, the mixture was transferred to a funnel and separation of the phases occurred. The oil phase was finally analyzed to determine the changes in the composition. It was found that the selected oxidants preferentially oxidized nitrogen compounds.

1.3.5.5 Extraction with conventional solvents

The use of conventional organic solvents preceded the research efforts on ionic liquids extraction. Solvent extraction comprises contacting the feed oil with a selected solvent in a vessel with adequate mixing for a determined time. The mixture is rapidly separated into two phases; a nitrogen rich phase which contains the extracted nitrogen compounds and the denitrogenated phase^{23, 30}. From the nitrogen rich phase, the solvent can be recovered by different methods including distillation or stripping.

Solvents such as methanol²³ and carboxylic acid²⁴ have been proposed in previous studies but their results were not satisfactory. Kodera et al. reported solvent extraction of nitrogen compounds from coal liquids using methanol and water as solvents in the process; the feed materials to the process were middle distillates of Wandoan and Battle River coal liquid with nitrogen contents of 0.51% and 0.42%, respectively. The percentage of extraction in the process increased with increasing the fraction of methanol utilized, reaching a maximum of around 50% for Battle River coal liquid. The optimal fraction of methanol was found for the process using model mixtures. As the fraction of methanol passed the optimum value, the selectivity for quinoline, isoquinoline, indole and carbazole in model mixtures were negatively affected.

Qi et al.²⁴ reported solvent extraction of nitrogen compounds from catalytically cracked diesel oil by using acetic acid solutions at various concentrations. The feedstock used in their study contained considerable amounts of nitrogen compounds (Total: 1520 ppm, basic: 148 ppm and non-basic: 1370 ppm). Acetic acid solutions with different concentrations were investigated. The results showed that the efficiency of the nitrogen extraction improved as the concentration of acetic acid increased. At 80% acetic acid concentration, the extraction efficiency was found to be optimum for the experiments and further analyses were carried out with this concentration. The percentage of extraction of nitrogen compounds also increased as the volume ratio of solvent to feed oil increased.

The recovery of the solvent was achieved by distillation up to 40°C under vacuum pressure (10mmHg) of the acid phase; this allowed separation of the solvent and the nitrogen compounds.

In their study, there is no information about the selectivity of the solvent for nitrogen over other compounds, however; the percentage of extraction and the distribution ratio of basic compounds were greater than for non-basic compounds.

CHAPTER 2:

Experimental

2.1 Feed Material and Chemicals

All of the chemicals used in the experiments are listed in Table 2-1. Heavy coker gas oil was the feed material used in the experiments. It was obtained from Syncrude Canada Ltd, derived from Athabasca bitumen by the fluid coking process. The main properties of the feed oil are shown in Table 2-2.

Table 2-1 List of Chemicals used in the experiments

Chemical	Manufacturer	Purity
Copper chloride dihydrate	Sigma Aldrich	99%+
<i>n</i> -Hexane	Fisher Scientific	95%
Dichloromethane	Fisher Scientific	
Hydrogen	PRAXAIR Canada Inc.	Ultra High Purity, 5.0
Argon	PRAXAIR Canada Inc	Ultra High Purity, 5.0
Water	N/A	RO
Never Seez	Bostik, NSBT-8	Regular Grade
Quinoline	Sigma Aldrich	98%
1-Methylnaphthalene	Acros organic	97%
Acetone	Sigma Aldrich	Cretified ACS
Toluene	Fisher Scientific	Cretified ACS

Table 2-2 Physical and chemical properties of the heavy coker gas oil ⁵⁹

Heavy coker gas oil	
Nitrogen (ppmw)	5463
Sulfur (ppmw)	40733
Specific gravity	0.98 @ 20 °C
Vapor pressure	1.9 psia @ 100 °C; < 1psia (Reid method)
Boiling range (°C)	220-620

2.1.1 Catalyst for hydrotreating

The catalyst used in this study was a commercially available Shell S424 Ni-Mo/ γ -Al₂O₃ hydrotreating catalyst. The estimated composition was: 2 – 4 wt % Ni and 12 – 15 wt % Mo. The surface area was measured as 158m²/g with an approximated pore volume of 0.39 mL/g. and bulk density 0.75 g/ML ⁶⁰. The catalyst was already presulfided. The presulfidization procedure is described in a previous study carried out at the University of Alberta ⁶⁰

2.2 Experimental equipment

2.2.1 Heating plate with agitation

An Isotemp Fisher Scientific hot plate stirrer was used in the complexation experiments to keep the feed materials at desired reaction temperature. The agitation speed was set to 700rpm.

2.2.2 Rotary evaporator

An IKA RV Control 10 rotary evaporator was used to remove the solvents from the product mixtures.

2.2.3 Nitrogen/Sulfur analyzer

A MultiTek™ horizontal N/S Analyzer system was used for characterization of the feed material and products. The Antek MultiTek™ system can be used for the detection of

nitrogen, sulfur and halides in solid, liquid, or gaseous materials. It can be used for either simultaneous nitrogen/sulfur analysis or halide analysis in a single instrument.

The principle of operation for nitrogen and sulfur analysis is based on chemiluminescence. The procedure for nitrogen and sulfur detection basically consists of oxidizing the nitrogen and sulfur compounds present in the sample using a high-temperature (1050°C) combustion tube. Oxidation products include CO₂, H₂O, •NO, SO₂, and various other oxides MOX. Oxidation of the entire sample matrix is illustrated in Equation 2-1. The combustion gases are routed through a membrane drying system to remove all water and then to the nitrogen and/or sulfur detector module(s) for quantitation.



The nitric oxide produced from this first step is subsequently contacted with ozone, produced by an on board ozone generator, to form electronically excited nitrogen dioxide NO₂*. The excited nitrogen dioxide emits light emitted at specific wavelength. This chemiluminescent emission is specific for nitrogen and it is proportional to the amount of nitrogen in the sample. The light emitted is detected by a photomultiplier tube (PMT). Only chemically bound nitrogen is detected; atmospheric, diatomic nitrogen (N₂) is not⁶¹



The SO₂ produced is exposed to ultraviolet (UV) radiation of specific wavelength as shown in equation 2-3. The UV radiation is re-released in the form of sulfur fluorescence. This fluorescence is proportional to the amount of sulfur in the original sample and can be detected by a photomultiplier tube (PMT)⁶¹



2.2.4 Thermal gravimetric analyzer

A Q500 Thermogravimetric analyzer from TA instruments USA was used to analyze the mass change of the copper chloride particles recovered as well as the nitrogen complexes formed during the complexation reaction.

2.2.5 Micro batch reactor

A micro batch reactor was used for the hydrotreatment experiments. The design of the micro batch reactor design is identical to laboratory reactors used in previous studies at the University of Alberta in experiments of hydroconversion⁶² and hydrotreatment⁶⁰. Figure 2-1 illustrates a schematic of the micro batch reactor of ~13 mL volume used in this study. This reactor was constructed with Swagelok parts and was assembled by the Chemical and Materials Engineering Department Machine Shop. The reactor body was made of 3/4" stainless steel tube, 1/16" thick and 5 cm long, with a 3/4" end cap for a bottom, and a 3/4" x 1/8" reducing union for a top. The neck of the reactor was a 1/8" stainless steel tube, approx. 7 cm long, with a 1/8" x 1/8" fitting at the end, which connected to the severe service valve⁶⁰. The reducing union at the top of the reactor neck was then connected to a Swagelok Severe-Service Union-Bonnet Needle Valve. This valve allowed for operation at temperatures up to 648 °C and working pressures up to 29.4 MPa at 400 °C⁶⁰.

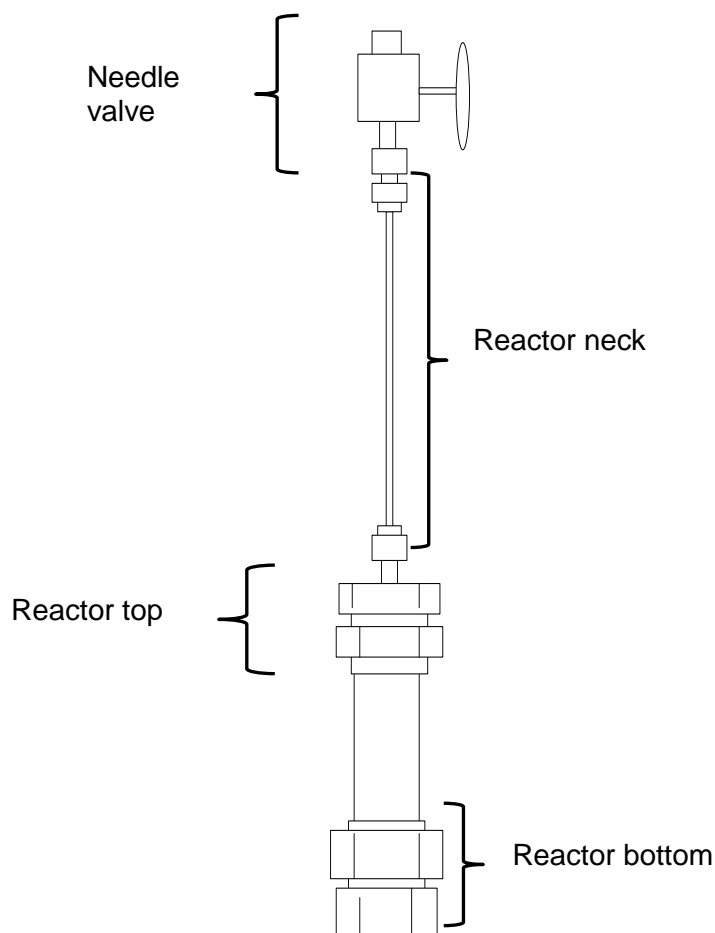
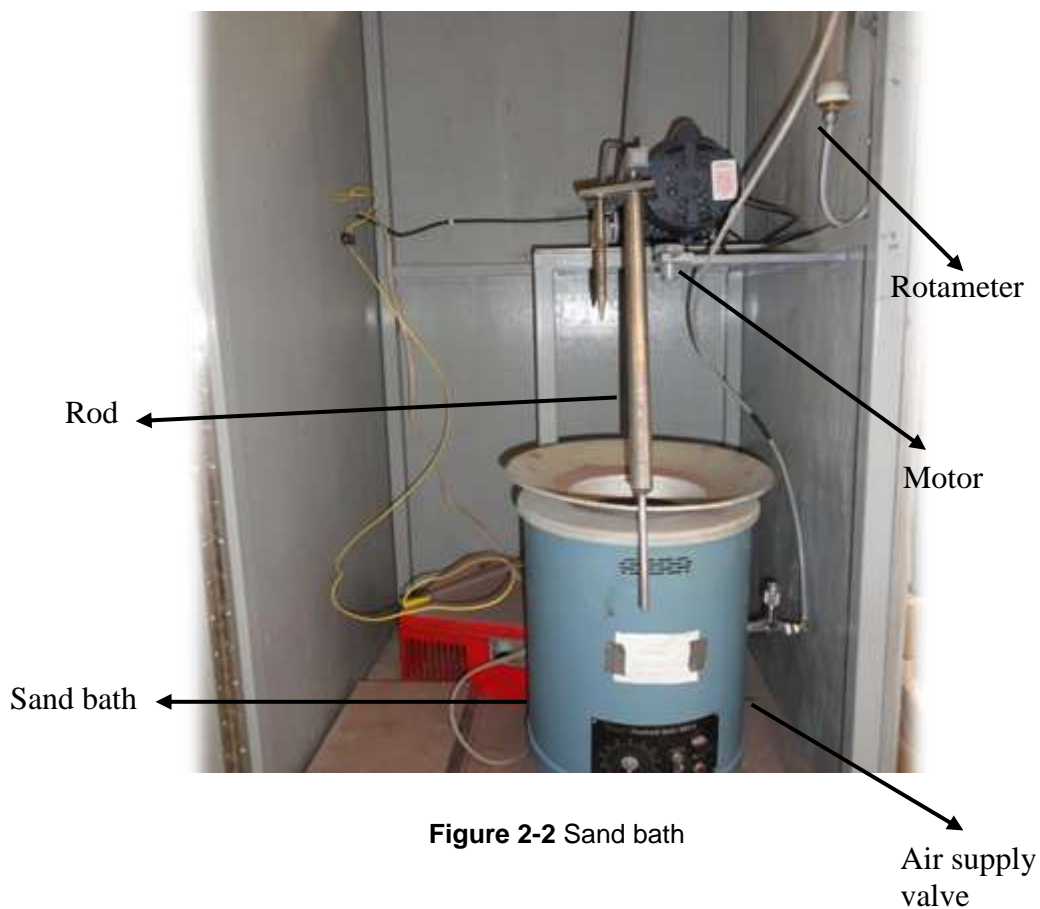


Figure 2-1 Schematic of the micro batch reactor

2.2.6 Sand Bath

The sand bath used to heat the micro reactor for the hydrotreatment reactions in this study was a Tecam Fluidized Sand Bath Model No. SBS – 4. A picture of the sand bath and its main components is shown in Figure 2-2.

The sand bath was filled with silica sand. A distributor located near the bottom of the sand bath allowed air to flow to the sand bath. An OMRON E5CK controller served to maintain the sand bath temperature to the desired set point value. The controller used a thermocouple as a sensor to measure the temperature of the sand bath at approximately the mid-point along the sand bath⁶⁰. A rotating cam powered by a motor was mounted above the sand bath; when running the experiments, the reactors were attached to a rod and immersed in the sand bath. The reactors were rapidly raised and lowered throughout the experiments.



2.2.7 Glove box

The hydrotreatment catalyst is very sensitive to oxidation and deactivation by contact with air. A Unilab-MBraun glove box was used during the experimental work to provide a reliable Argon atmosphere and avoid oxidation and subsequent deactivation of the catalyst. The component and parts of the glove box are shown in Figure 2-3.

The glove box used high purity Argon from an adjacent Argon cylinder to maintain an anaerobic environment (0.2 ppm of oxygen). One small chamber allowed laboratory equipment to be moved inside and outside the glove box. Pressure detectors and a pump regulated the internal pressure.

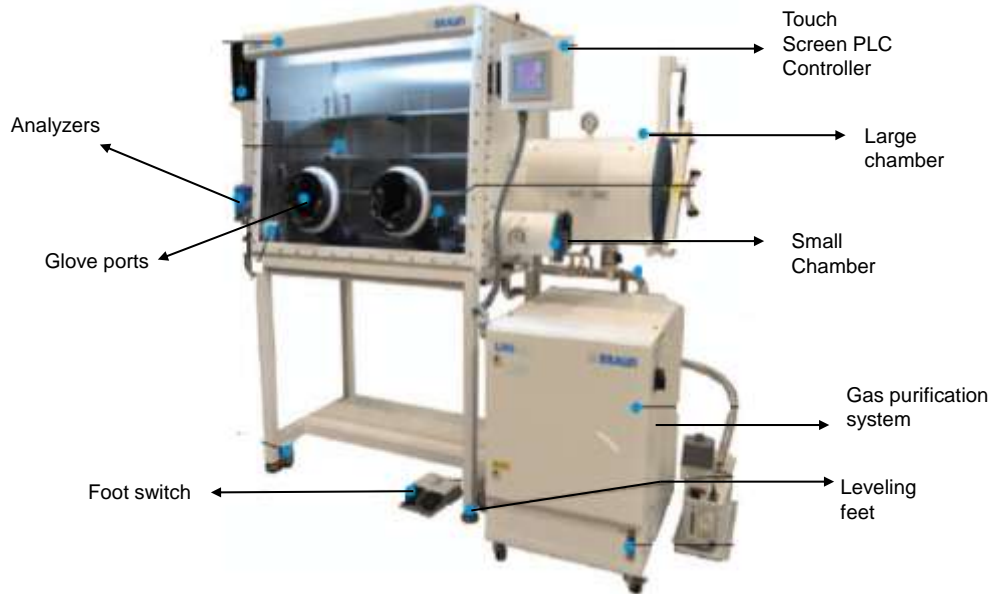


Figure 2-3 Unilab mbraun glove box ⁶³

The procedure for moving laboratory equipment into the glove box using the small chamber was as follows:

- It was verified that the pressure gauge in the chamber is reading 0, the inner door is closed, and the valve is in the closed position.
- The outer door was opened and the materials were placed on the tray. The chamber was sealed by closing the outer door.
- The chamber was evacuated by turning the valve to “evacuate”, the pressure was set below the pressure gauge. The materials were left for about 3 minutes.
- The chamber was refilled by turning the valve to “refill,” as indicated by the diagram. For non-porous materials, waited for the gauge to settle at the halfway point. The evacuation/refill procedure was repeated 3 times. The pressure was finally set to atmospheric pressure.
- The valve was turned to “closed” position. From within the glove box, the antechamber door was opened and the materials removed, then the antechamber door was closed.

The procedure for removing material from inside the glove box followed the same steps described above but in a reverse order.

2.3 Experimental procedure for nitrogen removal

The experimental procedure employed is illustrated in figure 2-4. The procedure is divided into 5 steps: reaction or complex formation, solids separation, solids recovery, oil recovery and nitrogen complexes recovery.

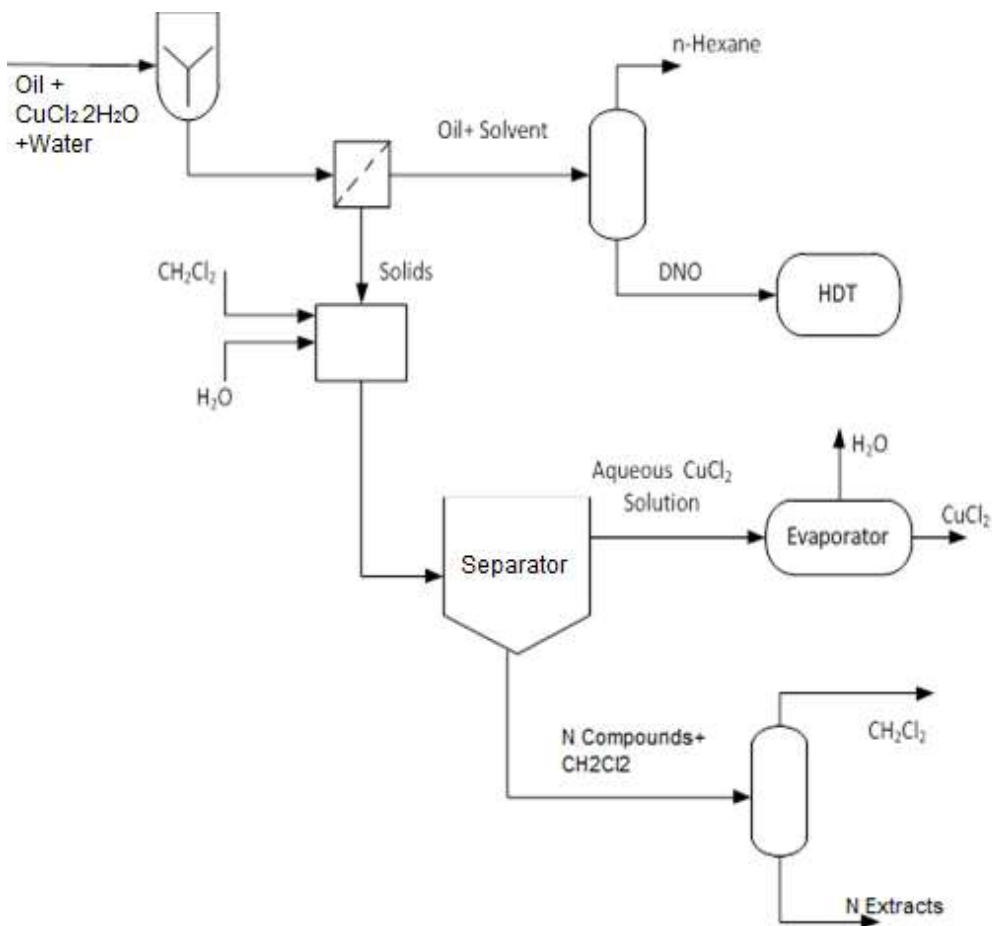


Figure 2-4 Schematic of the experimental procedure

2.3.1 Complexation reaction

Three different kinds of experiments were carried out to find the optimal composition of the metallic salt for the complexation step. A series of experiments using copper (II) chloride (anhydrous), copper (II) chloride dihydrate and copper chloride dihydrate plus additional extra water were carried out. Different copper chloride to feed weight ratios were also employed in these experiments.

The general procedure for these experiments was as follows. Approximately 10g of the feed material were placed in a 100ml round bottom flask. Subsequently, a defined mass of copper chloride was added to the reaction flask. The amount of copper chloride added for the reaction was necessary to get copper chloride to feed weight ratios of 0.2, 0.3 and 0.4. For the third set of experiments, when extra water was being added for the reaction, the required mass of water was added to the reaction flask preceding the copper chloride addition. The mass of water added for the reaction ranged between 0 to around 9wt%. These percentages were calculated by accounting for the total mass of water present in the reaction flask: hydration water and extra additional water.

Once the feed materials were loaded, the reaction flask was placed on a magnetic stirrer for 2h at 65°C and 700 rpm. After the reaction time was elapsed, *n*-hexane was added to the mixture to facilitate the separation of the solid particles from the oil by filtration. It was found that *n*-hexane washes the gas oil present on the surface of solid particles without dissolving the nitrogen containing compounds formed during the reaction. Solvent addition also helps to minimize the gas oil losses in the process. Separation of the copper chloride particles from the mixture by filtration was ineffective without addition of *n*-hexane. A second filtration was necessary to completely separate the solid particles from the mixture, further *n*-hexane addition served to precipitate the remaining solid particles in the liquid phase and to increase the copper salt recovery. The solid particles containing the copper salt and the nitrogen complexes were collected from the filter paper and stored for later treatment.

2.3.2 Solids-Oil separation

Once the complexation reaction was finished, approximately 30ml of *n*-hexane was added to the product mixture. Addition of solvent served to decrease the viscosity of the mixture and facilitate the filtration step. The products were vacuum filtered in a filtration system using 0.8 µm pore-size filter paper. Two more volumes of solvent were added to the flask throughout the filtration process. This solvent addition helped to remove completely the particles from the flask and mostly washed the gas oil remaining on the particles surface.

A second filtration step of the *n*-hexane/oil phase, previously recovered, was carried out using a 0.1µm pore size filter paper. This second filtration was necessary to completely remove the fine particles formed after the reaction. The products obtained after filtration were stored for future solvent evaporation.

2.3.3 Copper (II) chloride recovery

The recovery of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was attempted in two ways:

- The recovered particles were weighed to register the increase in mass after the reaction. 50 ml of dichloromethane (DCM) were added to a separation funnel where the recovered solid particles were placed. The funnel was mechanically agitated and the solvent quickly washed the nitrogen complexes off the particles surface. About 35ml of water were subsequently added to the mixture and the funnel was manually agitated once more. After about 10 minutes, two phases were separated, the oily phase containing the nitrogen compounds formed during the reaction and the aqueous phase containing the dissolved salt.

The bottom phase was partially removed from the funnel and stored in a container. The oil/water interface was not completely defined after the first water addition. Another 35ml of water were added to the funnel and the mixture was agitated. After 30 minutes, the two phases were again separated and the bottom phase was completely removed. The aqueous phase was filtered under vacuum conditions using a 0.1um filter paper. The filtration step was necessary to avoid any traces of oil coated fine particles that were not dissolved. The water from the aqueous phase was evaporated in a rotary evaporator until copper chloride anhydrous particles were obtained.

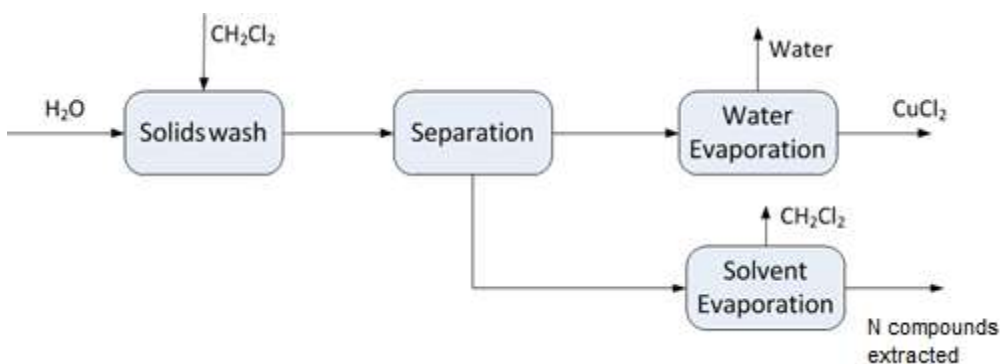


Figure 2-5 Schematic of the solids recovery- "Procedure a"

Dichloromethane was evaporated from the oily phase using a rotary evaporator. The nitrogen compounds formed during the complexation reaction were in this way finally separated. The N-containing compounds obtained were weighed and stored for further analysis.

In both evaporation procedures, the mass of final products was recorded at the end of the process. The products were subjected to further evaporation until it was found that the final mass did not differ from the previous measurement. In this way, we could be certain that no solvent remained in the final products.

- b. The solid particles were washed with a solvent capable of dissolving the N-containing compounds without dissolving the salt. Acetone and DCM were tested and both were effective in dissolving the nitrogen complexes.

The solid particles were weighed and subsequently placed in a flask. 50 ml of the selected solvent were added to the flask and the mixture was mechanically agitated. The mixture was subsequently filtered under vacuum conditions using a 0.22 μ m filter paper. After the first solvent wash, the nitrogen compounds on the solid particles surface were not completely removed. The solids collected on the filter paper after the first solvent wash were reprocessed two more times in the same fashion described previously. Once the washing process was finished, the product solids mostly recovered their initial blue color, indicating that the nitrogen complexes were essentially removed. The solvent was separated from the liquid mixture using a rotary evaporator and the N-containing compounds were collected, weighed and stored for further analysis.

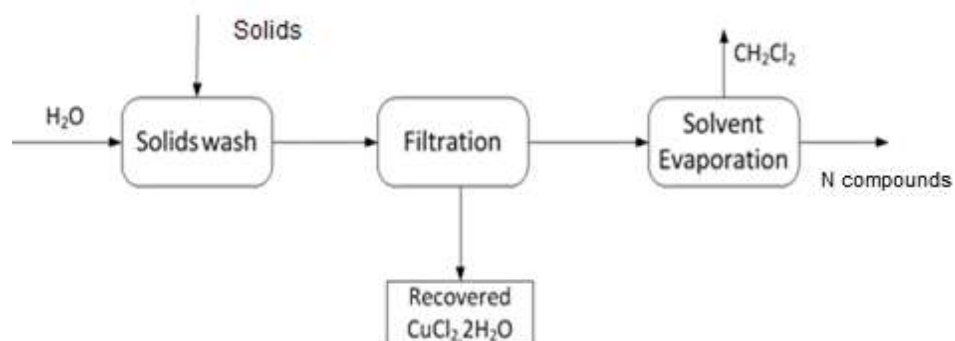


Figure 2-6 Schematic of the solids recovery- “Procedure b”

2.3.4 Recovery of the nitrogen compounds removed by complexation

The concentrated nitrogen compounds removed from the solid particles in the previous step were collected after solvent evaporation. The solvent evaporation process was conducted at 60 °C and the vacuum pressure was set according to the solvent employed in the recovery step. The evaporation flask was weighed before and after the evaporation

process to determine the mass of nitrogen compounds obtained in the process. Once the solvent was completely removed from the mixture, the flask was cooled down and weighed. The final mass was recorded. The product was once more subjected to evaporation for 1h and subsequently weighed to determine if there was any change in the final mass. This procedure was necessary to ensure that no solvent remained in the final product. Thermogravimetric analysis of the nitrogen compounds was carried out for some of the samples. The temperature program was the same as described in Section 2.3.5.

2.3.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of the recovered copper chloride particles as well as the nitrogen complexes was carried out in order to get a better understanding of the composition of the recovered particles.

The temperature program for the nitrogen compounds after solvent evaporation was set as follows:

- 1) 10 minutes, 29 °C isothermal under Nitrogen
- 2) 29 to 100 °C @ 5 °C/min under Nitrogen
- 3) 96 minutes, 100 °C isothermal under Nitrogen
- 4) 100-500 °C @ 10°C/min under Nitrogen/Argon.
- 5) 100 minutes, 500°C isothermal under air.

For the copper chloride particles before reaction and the copper chloride particles after recovery, the temperature program was as follows:

- 1) 10 minutes, 21 °C isothermal under Argon.
- 2) 21 to 100 °C @ 5 °C/min under Argon.
- 3) 96 minutes, 100 °C isothermal under Argon.
- 4) 100-500 °C @ 10°C/min under Argon.

Copper chloride particles before reaction were analyzed to find the temperature at which the particles start to lose the hydration water. This temperature was important for the recovery process.

2.3.6 Nitrogen and sulfur analysis of the feed material and denitrogenated oil (DNO)

The gas oil samples from all the steps in the process were individually analyzed for sulfur and nitrogen content. The analysis was carried out by chemiluminescence in an N/S

analyzer. In the beginning, the samples were sent to Canmet ENERGY's laboratory in Devon, AB, Canada. for the analysis, due to the lack of analytical capability at the University of Alberta. The procedure described here only refers to the analysis carried out at the University of Alberta laboratory.

The experimental procedure for all the gas oil samples analyzed was the following. First, the sample had to be dissolved with an appropriate solvent (Toluene for sulfur analysis and acetone for nitrogen analysis) to take the nitrogen and sulfur content to the desired range according to the calibration curve prepared.

A small volume of the gas oil sample was taken and weighed in a 30ml glass vial. The mass was recorded. Subsequently, a volume of solvent was added to the vial and the mass was recorded. Generally, the mass of the solvent added was about 12X the mass of sample employed for nitrogen determination and about 60X the mass of sample for sulfur determination. The vial was agitated to homogenize the contents and a portion of the diluted sample was moved to 1ml sample vial with septum. From these vials, the samples were easily taken by a syringe to be injected in the N/S analyzer.

The samples were injected in the sample boat of the Antek N/S analyzer. The volume injected was 5 μ l in all cases. Each sample was injected three times. The instrument software compares the raw sample data to the selected calibration curve to generate and report nitrogen and sulfur concentrations.

2.3.6.1 Calibration curves

The software has to compare the unknown sample data to calibration curves to report nitrogen and sulfur concentrations. Nitrogen and sulfur calibration standards were analyzed to produce individual calibration curves. The nitrogen and sulfur standard compounds chosen were carbazole and dibenzothiophene respectively.

A series of dissolutions of carbazole in acetone were prepared in different concentration levels ranging from 100 to 1000 ppmw of nitrogen. The calibration curve for sulfur was prepared using a series of dissolutions of dibenzothiophene in toluene, with concentration ranging between 150 to 1500 ppmw. The samples were run in the Antek N/S analyzer and the data was recorded. Linear response curves were obtained in these concentration ranges. Figure 2-8 is an example of one of the calibration curves obtained for nitrogen.

Control samples with known concentration values were run before starting the analysis of a new series of samples. The calibration curves were updated when the control samples were producing inaccurate values.

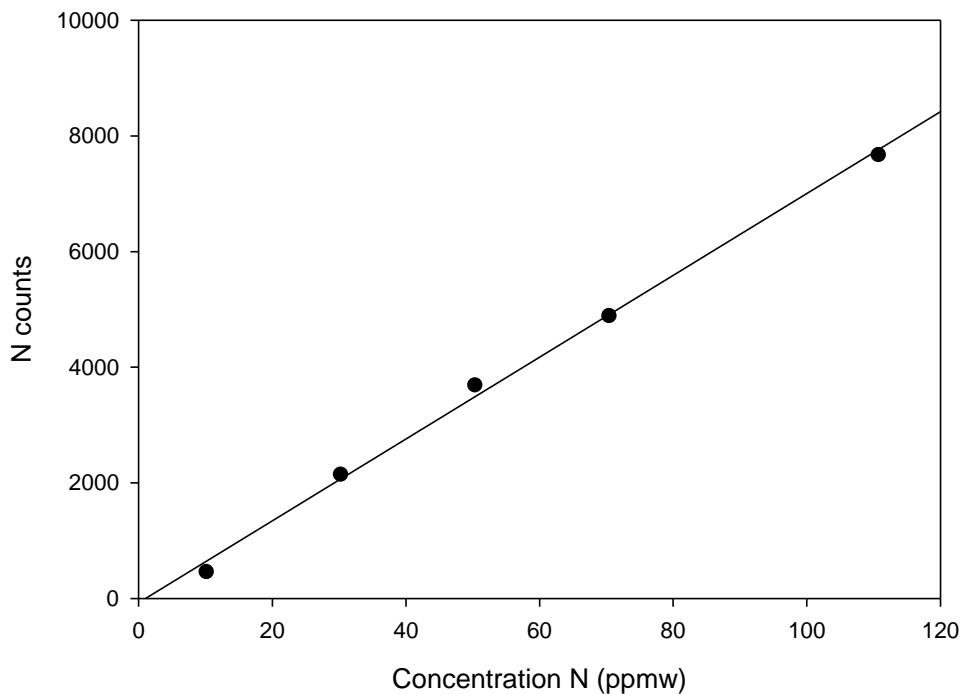


Figure 2-7 Example of a calibration curve for nitrogen

2.3.7 Micro-batch reactor loading

The feed to the micro reactor was added using the following procedure. The end cap of the reactor was loosened and subsequently, the micro-reactor was placed inside the glove box without the reducing union at the top of it. Once inside the glove box, the bottom half of the reactor with the top opened was placed onto a scale. The feed oil was carefully added to the reactor, circa 1g, using a spatula. Presulfided catalyst was then added to the reactor. Finally, two small stainless steel mixing balls, 4 mm in diameter, were added to the reactor to promote mixing. The reactor cap was fastened to the bottom by hand, the reducing union was connected back to the reactor and the valve was closed. Once the micro-reactor was successfully loaded with the feed, the reactor was removed from the glove box and taken to the lab for pressurization.

Two different types of feed material were used for the experiments: The first one was the untreated gas oil sample; the second one was the denitrogenated gas oil obtained under

the highest nitrogen removal conditions. These experiments were performed to give us a comparison basis and to assess the impact of removing high quantities of nitrogen species prior to hydrotreatment. The reaction conditions for both types of feed were identical.

2.3.8 Micro batch reactor sealing and pressurization

The top of the micro-reactor was loosened, and the female nut lifted to apply sealant. Never Seez sealant was applied to the threading of the reactor top. The sealant promotes a more effective seal, helping to prevent leaks, and makes easier the process of opening the reactor after reaction. The reactor was then closed by tightening the top of the reactor with a bench vice and wrench.

After the reactor was sealed, it was connected to the H₂ cylinder with the valve apparatus shown in Figure 2-4. The H₂ cylinder valve (V1), H₂ supply valve (V2) and the reactor valve (V3) were moved to open position so hydrogen could flow inside the micro-reactor. Once pressurized, the reactor fittings were check for possible leaks. A leak detection fluid, which consists on a mixture of water and snoop was applied to the fittings. After the leakage checking was passed, essentially absence of bubbles formed by the fluid; the reactor valve was set to closed position, the cylinder valve was also closed and the reactor disconnected. The reactor was subjected to three filling/ purge cycles before reaction for all the experiments.

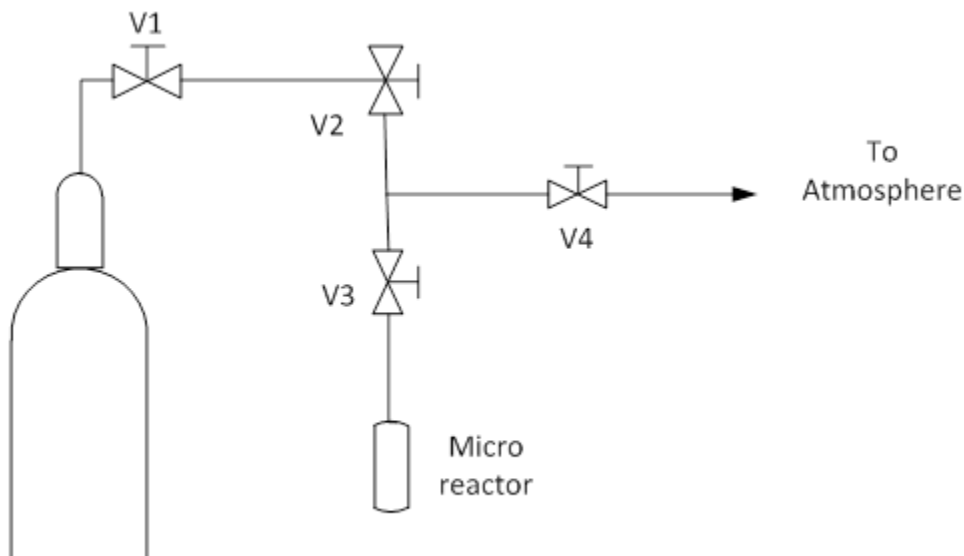


Figure 2-8 Schematic of the micro reactor valve set-up

2.3.9 Hydrotreating Reaction

After the reactor was successfully sealed and pressurized with H₂ at 4000 kPa at room temperature, the reactor was attached to the rod in the sand bath. The rod/ micro reactor were subsequently immersed in the sand bath and the motor was turned on. The shaking of the reactor promotes good mixing inside the reactor and maintains a homogeneous temperature.

The conditions for all the experiments performed in this study were 380 °C and 4000 kPa for 20 minutes, and 0.1 catalyst to feed weight ratio. Once the reaction time elapsed, the reactor was lifted from the sand bath, removed from the rod and quenched with water. The product gases were released into a fume hood, after the reactor cooled.

2.3.10 Product recovery from hydrotreatment reaction

After the product gases were vented, the reactor was placed in a bench vice and the top end of the reactor loosened, but not unsealed. The reactor was subsequently moved inside the glove box along with a 20 mL glass beaker and a square fabric metal mesh. The reactor was then unsealed by manually removing the top half of it.

Toluene was added to the reactor. The products were drained through the mesh and collected in the beaker. The reactor was carefully rinsed two more times with solvent to make sure that all the contents were removed. The filtered catalyst particles and the mesh were cautiously rinsed to remove all the oil present on their surface.

The micro reactor and the liquid collected in the beaker were then removed from the glove box, the catalyst was left to dry inside the glove box. The liquid mixture had residual catalyst fines which had to be removed before further analysis of the samples. This procedure was carried out using a 5 mL plastic syringe with a 0.2 µm filter. The filtered sample was then placed in a 10ml evaporation flask and the solvent was then evaporated using a rotary evaporator for 2h or until there was no change in the mass recorded in the previous measurement. The product oil was then carefully collected into a vial to be stored for nitrogen and sulfur analysis.

2.3.11 Nitrogen and sulfur content analysis

The product oil collected from the previous step was analyzed for sulfur and nitrogen content. The samples were weighed and dissolved using either acetone or toluene depending on the required measurement.

A 20 ml vial was placed onto a balance. A small quantity, normally circa 0.08g of the oil sample was added to the vial and the exact mass was recorded. Subsequently, solvent was added to the vial to dissolve the oil. Dissolution of the oil sample was needed to get the nitrogen and sulfur content to the desired range according to the calibration curve prepared. The mass of solvent added was also recorded. A portion of the diluted sample was transferred to 1ml sample vials with septa. From these vials, the samples were easily taken by a syringe to be injected in the N/S analyzer.

The amount of sample injected in the sample boat was 5 μ l in all the cases. Each sample was injected three times. If the measurements for the same sample significantly differed in the three injections, the sample was prepared and injected again in the same fashion described above.

CHAPTER 3:

Results and discussion

In this chapter, the results from the experimental work are summarized and discussed. First, the effect of variables such as: salt to oil weight ratio and the percent of total water in the mixture on the nitrogen and sulfur removal efficiency are analyzed. Subsequently, the effect of the reaction time is also discussed. A close look to the content of basic and non-basic nitrogen species in the sample gives an idea of the compounds that are being targeted during the reaction. Finally, the recovery of the copper chloride particles and separation of the nitrogen compounds formed during the reaction is approached.

3.1 Removal of nitrogen compounds by complexation

3.1.1 Effect of salt to oil weight ratio and salt composition

The nitrogen removal efficiency at different salt to oil weight ratios, for the three different kinds of experiments (copper chloride anhydrous, copper (II) chloride dihydrate and copper (II) chloride dihydrate + different percentages of water (5-10 wt%)) are shown in Figure 3-1. Throughout this chapter, “copper (II) chloride” will refer to copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) unless otherwise indicated. The reduced particle size copper chloride was obtained by crushing the salt using a mortar and pestle tool. The most important finding is that increasing the salt to oil ratio for the reaction does not have much influence on the nitrogen removal efficiency; however, the composition of the salt has a more significant impact. If extra water is added in the reaction step, the nitrogen removal efficiency is highly enhanced. The trend on the figure shows a considerable difference on

the nitrogen removal efficiency when water is added for the reaction in comparison to the other two cases.

The molar ratios of Cu to N in the experiments were 3.0, 4.5 and 6.0 for 0.2, 0.3 and 0.4 salt to oil weight ratios, respectively. If we take as an example the reaction of copper (II) chloride with pyridine (Equation 1-3); the stoichiometric ratio of Cu to N in the reaction is 1:1. The amount of copper fed for the experiments guaranteed that at least for the pyridine reaction we have an excess of copper. Due to the great variety of nitrogen species present in the oil, the stoichiometric ratio of Cu to N for all the reactions taking place is uncertain. Increasing the mass ratio of copper salt to oil in the reaction results in a higher molar ratio of the species of interest but it was demonstrated that the effect of this variable is not as important as addition of free water.

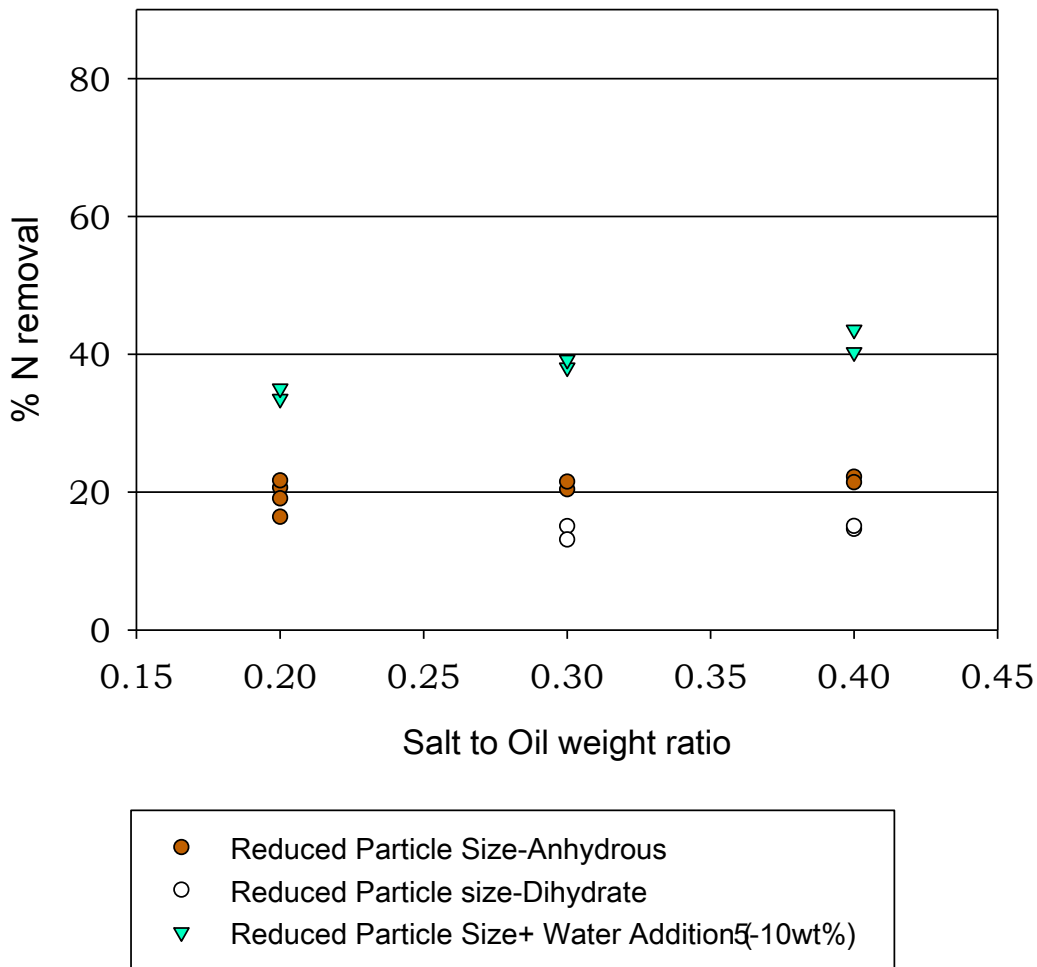


Figure 3-1 Effect of salt to oil weight ratio and salt composition on nitrogen removal efficiency.

The set of experiments with copper (II) chloride showed lower efficiency of nitrogen removal in comparison to the anhydrous form of the copper chloride. These results disagree with the previous results found in the literature ¹⁶.

The lower nitrogen removal efficiency can be explained by two different situations: The first one is that when using the anhydrous form of the copper salt, the particle size of the solids is reduced. The smaller particle size gives a larger contact area between the oil and the salt and enhances the removal process efficiency. The second one is a difference among the three experiments. The filter paper that was first being used in the filtration step (0.8 μm), did not allow an adequate separation of the solids from the oil after reaction. The remaining solid particles in the oil phase contain the nitrogen complexes formed on their surface and these species are included when analyzing the product oil for nitrogen.

Due to the inefficient separation, it was decided to change the filter paper in the filtration step to a smaller pore size filter paper. The pore size was improved from 0.8 μm to 0.22 μm for the set of experiments 2 and 3 (Anhydrous and addition of extra water). The smaller pore size filter paper produced a better solid particle-oil separation. Given the substantial difference in the results when extra water is added for the reaction, it was decided that repeating the experiments with copper chloride dihydrate and the smaller pore size filter paper was not necessary. The results illustrated a key major modification necessary for a more successful extraction process.

The results can also be visually represented; the solid particles recovered from the product mixture after the reaction were observed under an optical microscope. The three pictures shown below were obtained at 4X magnification. Figure 3-2 is an image of the copper chloride dihydrate particles before reaction, showing distinct blue-green needle-shaped crystals. Figure 3-3 is an image of the copper chloride dihydrate particles obtained after reaction and filtration and finally, Figure 3-4 was obtained from the copper chloride dihydrate particles after reaction and filtration when extra water was added for the reaction.

A comparison between the three microscope images quickly gives an idea of the improvement in the complexation process. The nitrogen-copper chloride complex appears as distinct small brown-colored particles. In the absence of excess water, the complexes must form at the liquid-crystal interface. Figure 3-3 shows that the complexes formed on the particles surface are more homogeneously distributed when water is added to the reaction flask. The addition of water helps to dissolve some of the

solid copper particles which facilitates the contact between the copper salt and the oil components at the interface.

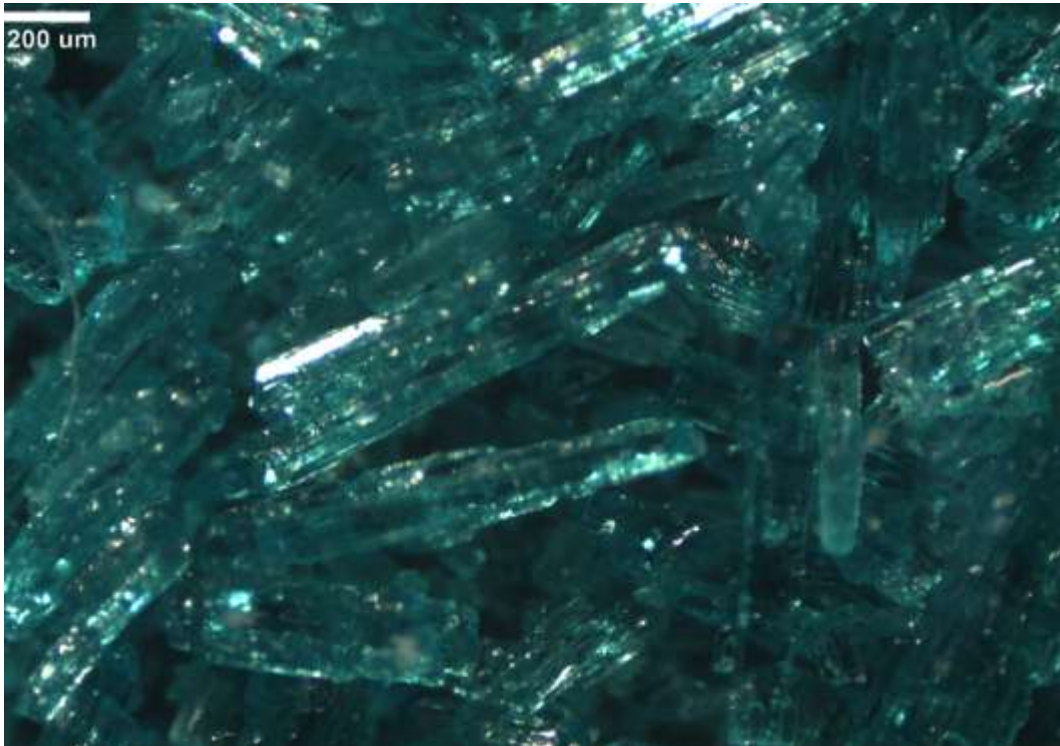


Figure 3-2 Copper salt dihydrate before reaction

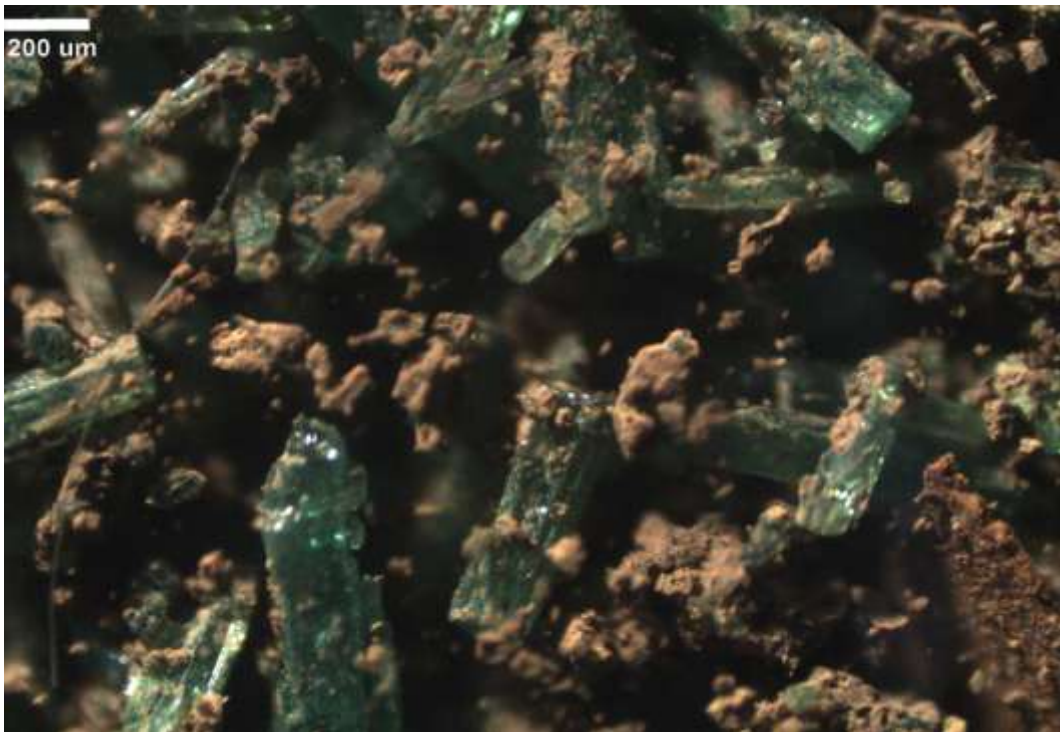


Figure 3-3 Copper salt after reaction



Figure 3-4 Copper salt after the reaction (addition of 5.1 wt% water)

3.1.2 Effect of the amount of water on nitrogen removal efficiency

Addition of extra water was found to be critical in the nitrogen removal process. A series of experiments using a 0.2 salt to oil weight ratio and different percentages of total water were conducted. The purpose of these runs was to determine the optimum proportion of water to get the highest nitrogen removal efficiency during the reaction. The percentage of water in the mixture was calculated taking into account the hydration water and the extra water added as follows:

$$\% \text{ Water in the mixture} = \frac{0.21 * \text{Mass of } \text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{Mass of extra water}}{\text{Mass of (Oil + } \text{CuCl}_2 \cdot 2\text{H}_2\text{O + extra water)}} * 100$$

The trend shows that the removed percent increases significantly as water is added and it reaches a limit at around 9% of total water content in the mixture (Figure 3-5). Addition of water beyond values of 8.6%wt makes difficult the separation of the solid particles after the reaction. The theoretical nitrogen removal limit is expected to be the percentage of basic nitrogen compounds present in the initial oil. At the maximum removal efficiency,

the molar ratio of Cu to N is 3:1. This molar ratio guarantees excess of copper for the reaction.

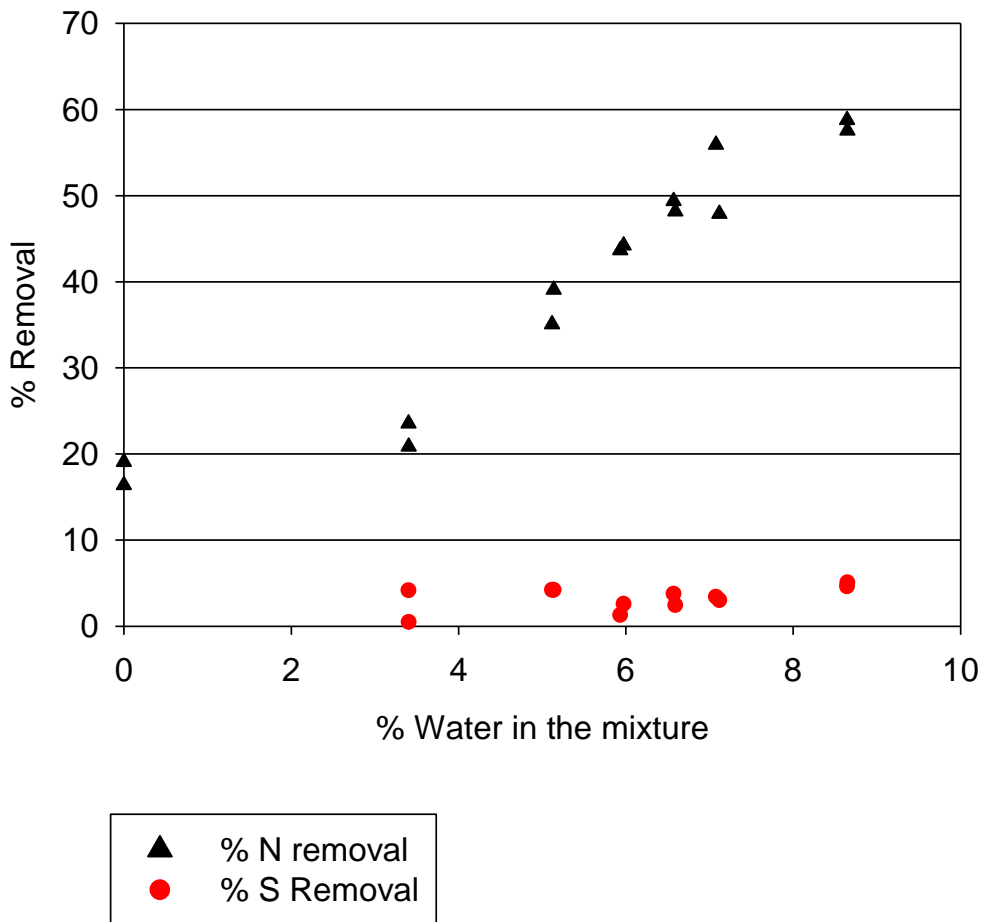


Figure 3-5 Effect of the % total water in the reaction mixture on nitrogen removal efficiency.

The high selectivity of copper chloride for nitrogen over sulfur compounds was confirmed by sulfur analysis of the oil samples after reaction. The sulfur content of the oil remained almost constant after the reaction. Increasing the percentage of total water in the reaction also did not affect the content of sulfur in the oil samples.

Addition of water embodies an improvement over the previous research reports in terms of nitrogen removal capacity. Narangerel and Sugimoto⁹ were able to remove up to 63% of the nitrogen species from bitumen-derived light gas oil; the initial content of nitrogen in

their oil was around 20% of the nitrogen content of the gas oil in this study. Also, the Cu to N molar ratio used was 3.25 times larger than in this study. When they changed the feed oil from bitumen-derived gas oil to shale oil, the nitrogen removal efficiency was increased to 88%. The highest removal efficiency when using shale oil can be explained by the difference in composition with respect to bitumen-derived oils. Shale oil was found to have different species distribution and higher content of basic nitrogen. Choi and Dines¹⁶ also achieved very high nitrogen removal rates (~85%) using copper chloride dihydrate with shale oil as feed material; their results are similar to the ones by Narangerel and Sugimoto for shale oil.

Figures 3-6 and 3-7 were obtained by an optical microscope at 10X. A sample from a reaction mixture of copper chloride dihydrate, water and oil was taken from the reaction flask and observed under the microscope. The images give an idea of what is happening inside the reaction flask when water is present.

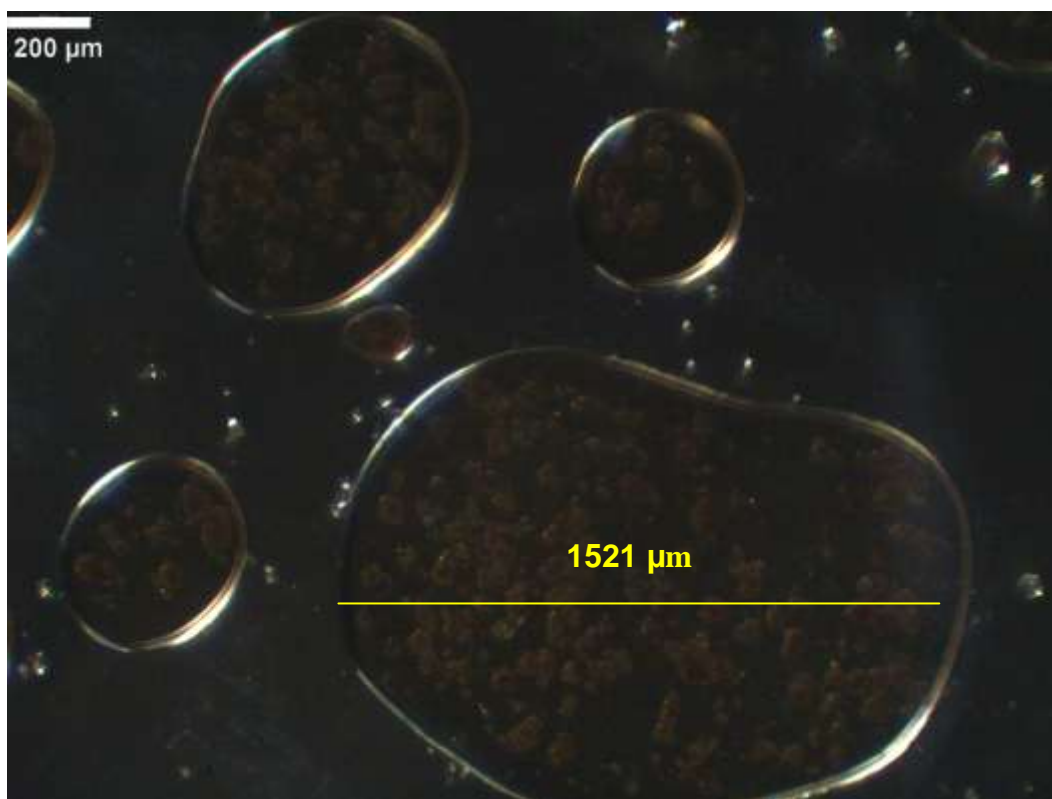


Figure 3-6 Microscope image of a reaction mixture when 8.65wt% water is added

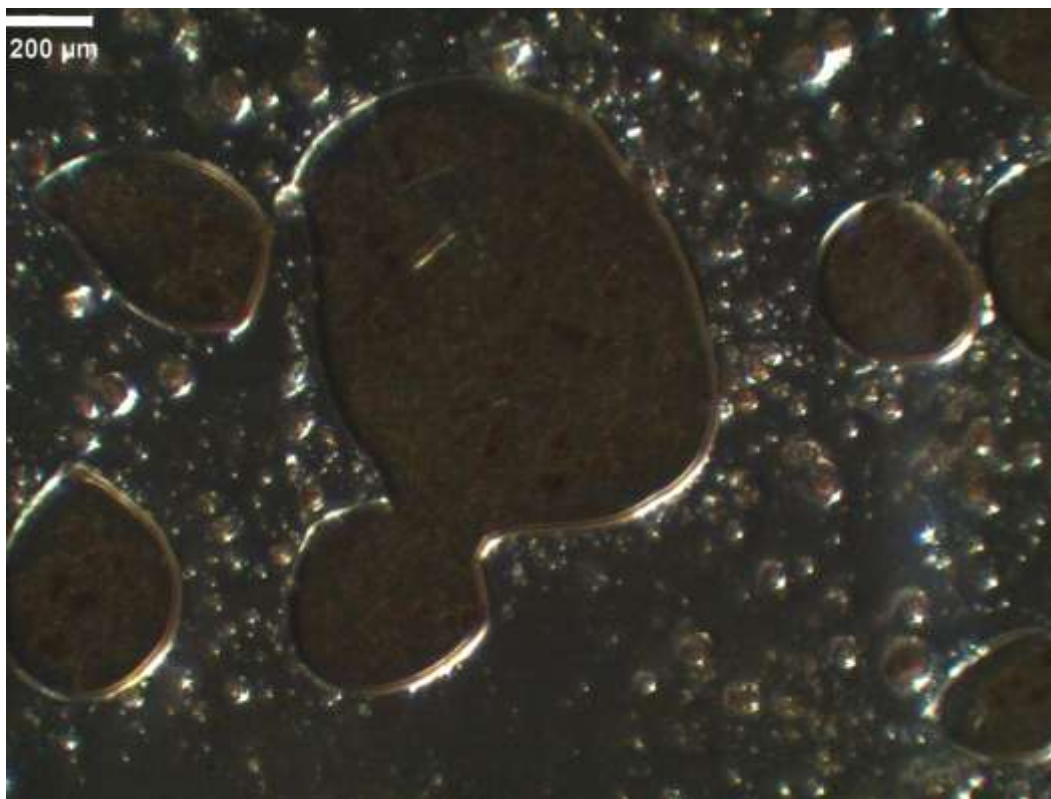


Figure 3-7 Microscope image of a reaction mixture when 8.65 wt% extra water is added

The water in the mixture partially dissolves the copper chloride crystals and the surface area available for reaction is increased. Both micrographs show evidence of copper chloride crystals within the aqueous droplets. The aqueous copper chloride solution forms small emulsion domains where the copper ions are readily available to react with the nitrogen compounds present in the oil, which is the continuous phase in these images. When the nitrogen species and the copper ions encounter each other at the interface, the reaction occurs. The nitrogen complexes formed during the process, slowly accumulate on the surface of the non-dissolved copper chloride particles and remain inside the aqueous copper chloride solution domains.

Figure 3-8 is a representation of the interface during the complexation process. The addition of extra water forms a saturated aqueous film that is in contact with the oil phase. The copper cations are readily available for the nitrogen species to interact and the water in the reaction provides a renewable contact area.

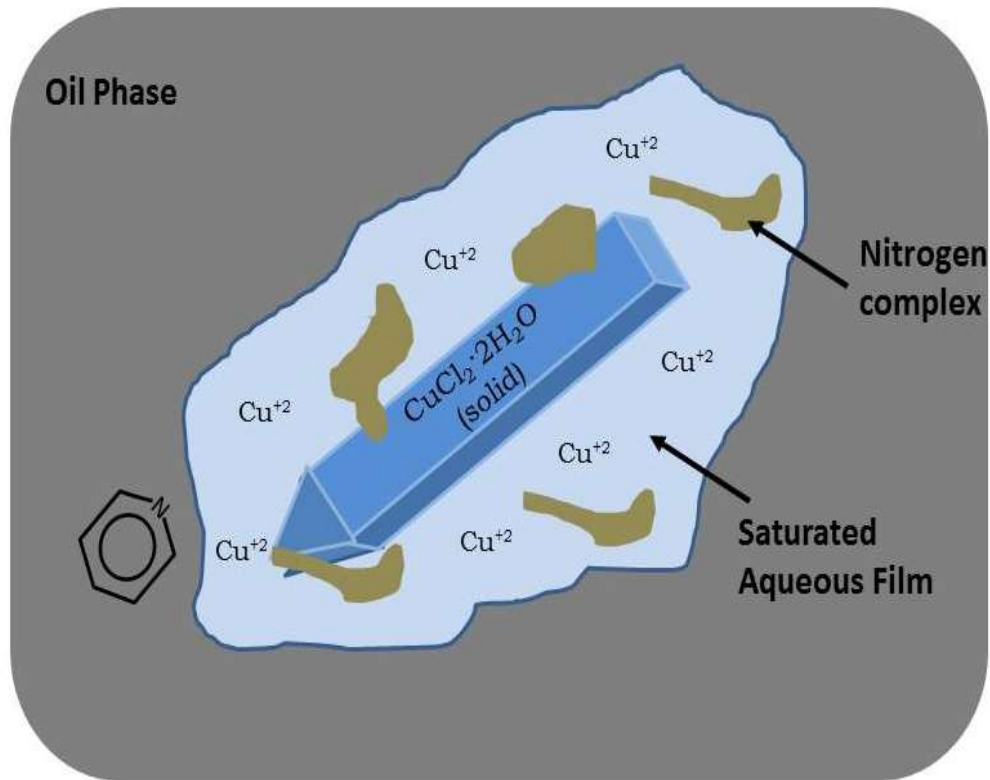


Figure 3-8 Schematic of the interface during the complexation reaction

A sample of synthetic oil was used as feed material to run a blank experiment. Figures 3-9 and 3-10 are images obtained from a sample of reaction mixture of synthetic oil (paraflex), copper chloride dihydrate and extra water. From these images, it can be seen that the aqueous copper chloride islands surround solid copper chloride crystals within a continuous oil phase. In this case, accumulation of dark particles inside the domains, due to the nitrogen complexes formed by reaction, is not observed.

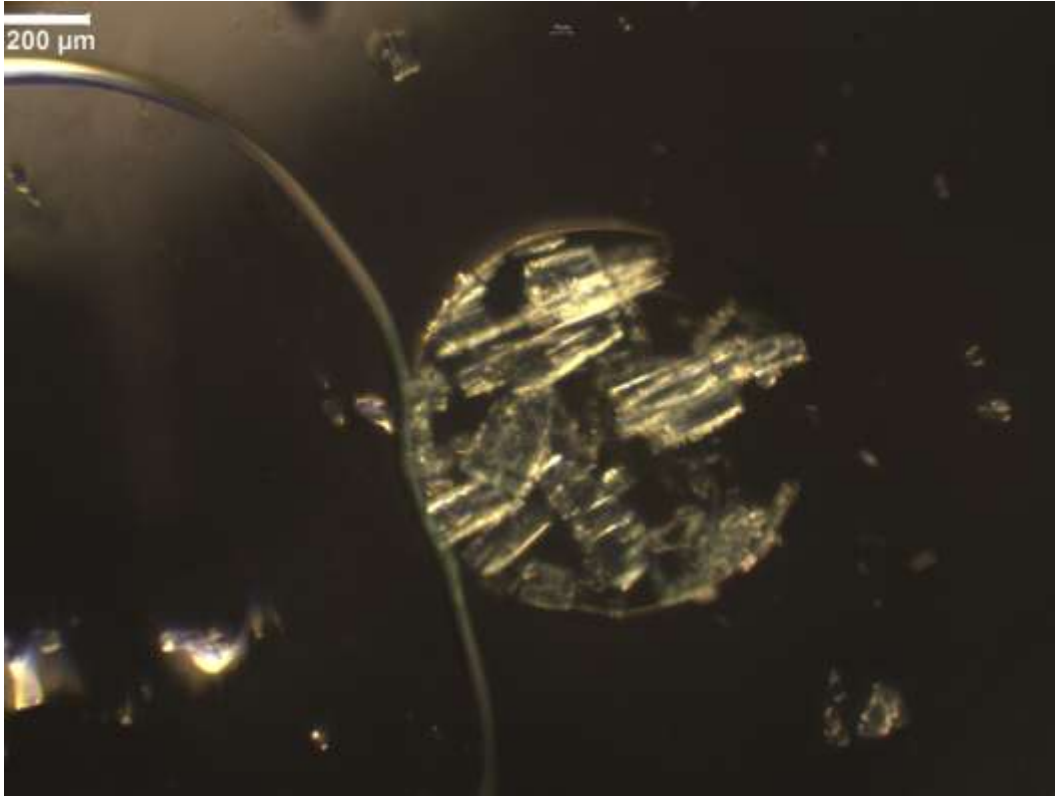


Figure 3-9 Microscope image of a blank mixture when 8.5wt% extra water is added

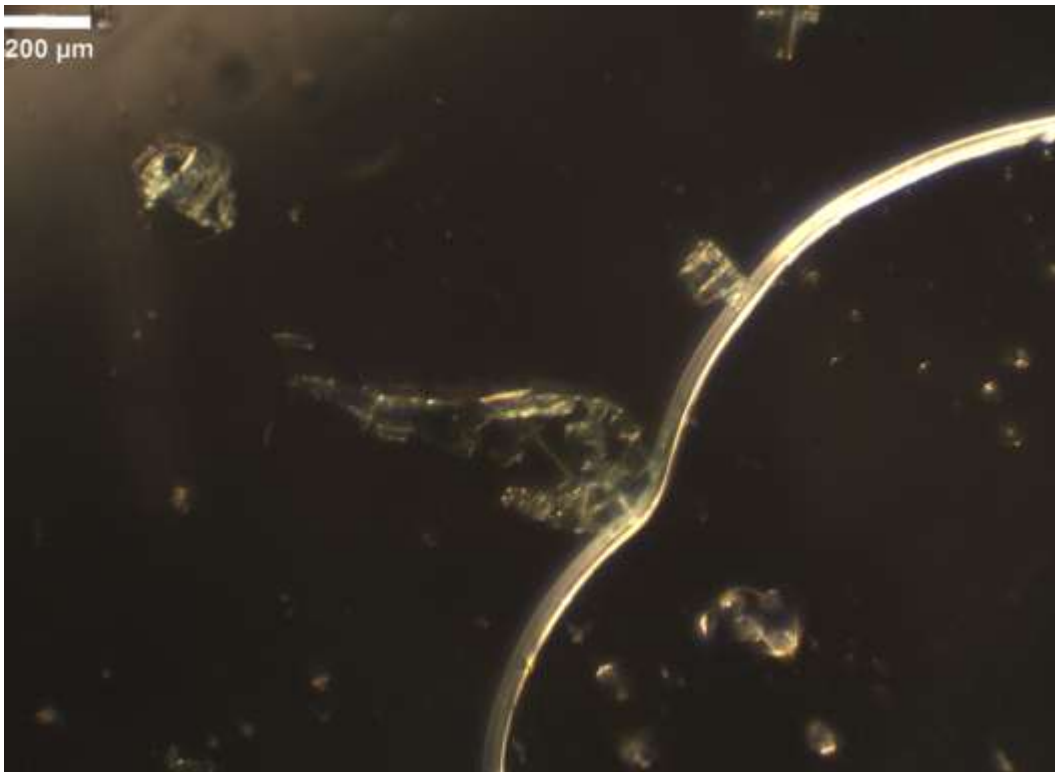


Figure 3-10 Microscope image of a blank mixture when 8.65 wt% extra water is added

3.1.3 Effect of the reaction time

The effect of the reaction time was investigated. In previous studies; investigators found that 2 hours reaction time is required for the reaction to reach completion. A series of experiments with copper chloride and the feed oil were run at the best reaction conditions previously found in this study: 65°C, 0.2 salt to oil weight ratio and 8.6% total water in the mixture; the reaction duration was varied from 30 to 150 minutes.

The trend shown in Figure 3-11 is that as the reaction time increases, the nitrogen removal efficiency increases linearly until 120 minutes. At 150 minutes reaction time, the nitrogen removal percentage does not increase any further in comparison to the previous data point. These results agree with the previous findings, 2 hours reaction time is sufficient for the complexation reaction to reach equilibrium at the selected temperature and mixing conditions.

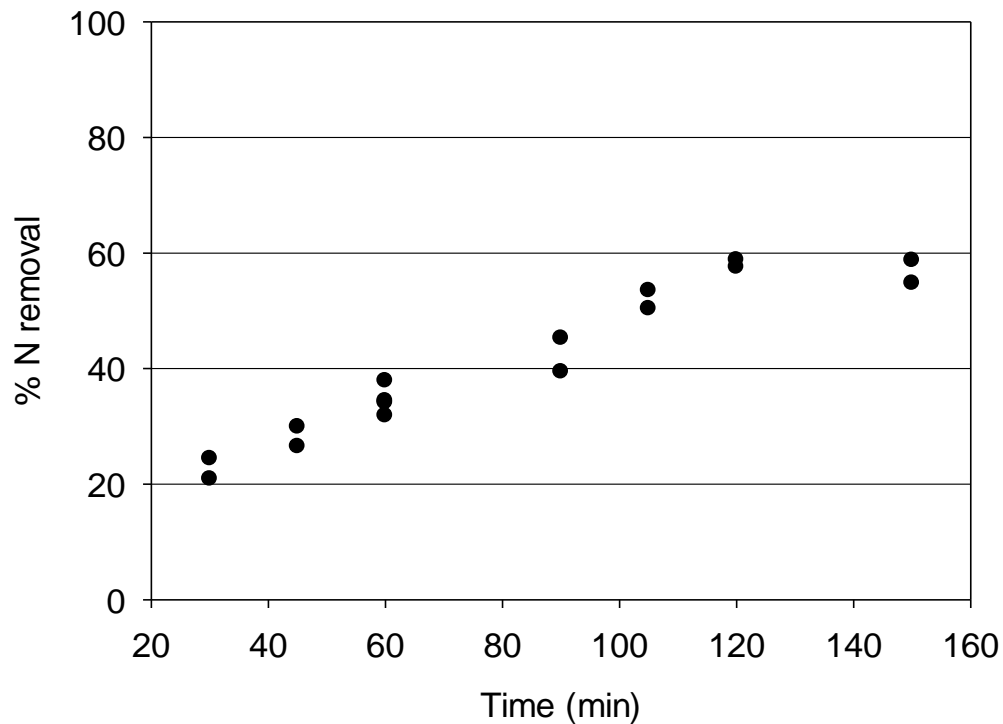


Figure 3-11 Effect of the reaction time on the nitrogen removal efficiency.

3.1.4 Basic and non-basic nitrogen in the oil samples

The content of basic and non-basic nitrogen species on the oil samples before and after the reaction was analyzed. The samples were analyzed using the standard method ASTM D2896 at the Canmet Energy Technology Centre laboratory in Devon, AB. The results of this analysis (Table 3-3) show that the initial content of basic nitrogen species on the original oil samples is around 30%wt of the total whereas; the content of basic nitrogen species on the denitrogenated oil samples is negligible. The results confirm that complexation with copper chloride removes 100% of the basic nitrogen species. The data also show that the non-basic nitrogen compounds present in the feed material are also removed.

Table 3-1 Basic nitrogen content on the oil samples

Sample	Description	Basic N, mg/kg	% of total N
1	Untreated heavy gas oil	1674.4	30
2	Untreated heavy gas oil	1610.2	30
3	Denitrogenated Oil (DNO)	0.00	0
4	Denitrogenated Oil (DNO)	0.00	0

Based on the total nitrogen content shown in table 2-2 (5433ppmw), the removal efficiency of the non-basic nitrogen was circa 45%. This result was unexpected, because the carbazole-indole type components in the gas oil do not have free electrons available to form donor-acceptor complexes.

The fraction of basic nitrogen species in the oil sample in this study is in the same range as the basic nitrogen fraction found in different bitumen derived oils in the literature^{9, 38, 64}, for example: Ferdous et al⁶⁴ indicated a fraction of 35% basic nitrogen of the total nitrogen in heavy gas oil derived from Athabasca bitumen. Narangerel and Sugimoto⁹ established that the gas oil for their experiments contained 39% of basic nitrogen of the total nitrogen content.

3.2 Copper chloride recovery

The nitrogen complexes formed on the solids surface were removed by addition of dichloromethane and water as previously described in section 2.3.3. In this way, the copper chloride particles could be separated and recovered from the process.

The efficiency of the recovery process was assessed in terms of fraction of the initial mass recovered. The calculation was based on the mass of the particles fed to the process and the mass of particles obtained at the end of the process. The results of some of the recovery experiments are shown in Table 3-2. Unfortunately, from the results, a correlation between the percentages of water in the reaction or the reaction time with the percentage of recovery cannot be obtained. The reason for this is that the salt recovery experiments were attempted as a final step in the process. As previously discussed, two different procedures were used. The solids samples were randomly taken and subjected to either procedure a) or b). The results in Table 3-2 are only useful to illustrate that high recovery percentages can be achieved for the solids in the process using procedure a)

Table 3-2 Percentage of solids recovery for various experiments using procedure a)

Experiment	Mass of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ fed (g)	Mass of CuCl_2 recovered* (g)	Mass of CuCl_2 recovered** (g)	% Recovery
1	2.0023	1.5641	1.9844	99.11
2	2.0016	1.4150	1.7952	89.69
3	2.0022	1.5148	1.9218	95.99
4	2.0021	1.5182	1.9262	96.21
5	2.0043	1.5130	1.9196	95.77
6	3.0006	2.2844	2.8982	96.59
7	2.0010	1.5714	1.9937	99.63
8	2.0048	1.5290	1.9399	96.76

*Recorded after evaporation of water (anhydrous particles)

** Calculated based on the hydration water content and the mass of CuCl_2 recovered

Thermogravimetric analysis (TGA) allows us to assess the change of the mass of samples with temperature. This analysis provides valuable information for the process. Figure 3-12 shows the results of a TGA run for the copper chloride particles before reaction. The analysis confirmed the theoretical amount of water associated to the particles. According to Figure 3-12, the content of water in the salt particles was 21 wt%,

consistent with the dihydrate. The graph also indicates the temperature at which the particles start to lose the hydration water. Under inert atmosphere, the mass loss starts at around 45°C; when the temperature reaches 100°C; all the hydration water is gone.

The information obtained from TGA was useful in the solids recovery step. During water evaporation from the copper solution, the temperature of the rotary evaporator was 60°C. This temperature is above the temperature for water loss from the dihydrate. Due to the higher set point temperature in the evaporator, it was decided to remove all the water from the aqueous solution and also the hydration water until anhydrous copper chloride particles were obtained. The final mass of copper chloride anhydrous was measured and the mass of copper chloride dihydrate recovered in the process could then be calculated.

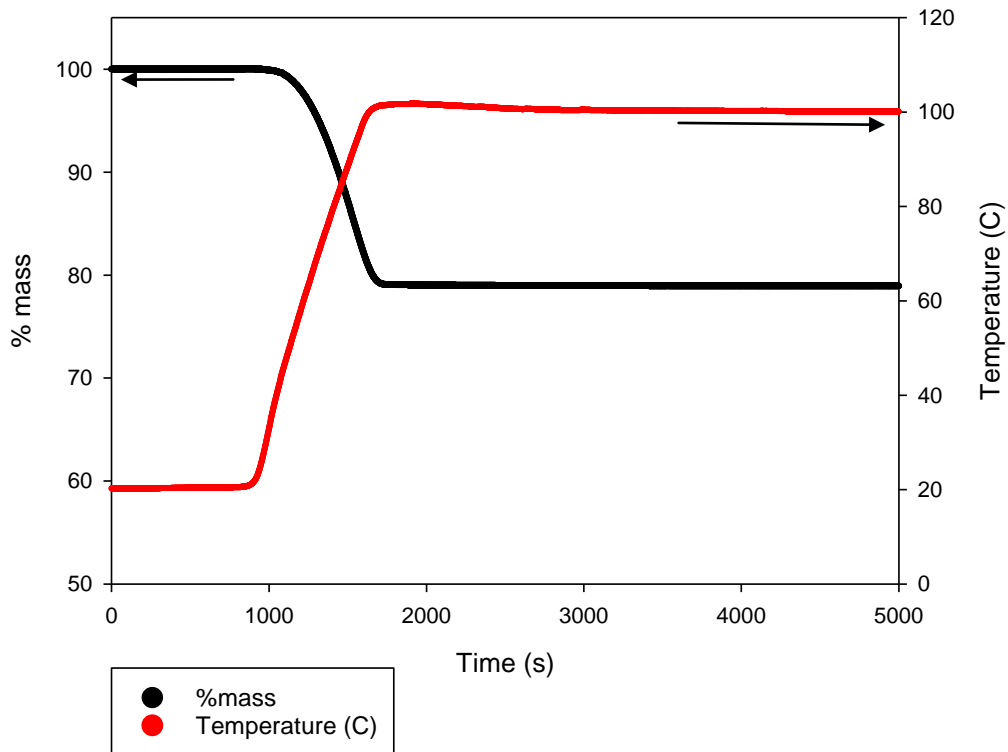


Figure 3-12 Decomposition of as-received copper chloride dihydrate by TGA in Ar

The starting point of the solids recovery process is to separate the copper chloride crystals and particles of copper complex from the oil after the reaction is stopped. Thermogravimetric analyses of the copper chloride particles, the product of the reaction, allowed investigation of this material under an inert atmosphere while the temperature

was gradually increased to reach 500 °C. Figures 3-13 and 3-14 are from reaction products samples taken after filtration.

The trends in both figures show that approximately half of the initial mass of the samples is lost in the analysis. The first mass loss portion observed in Figure 3-13 is probably due to some small amount of solvent trapped inside the particles; this behaviour is not observed in Figure 3-14. The second mass loss portion is due to the water present in the particles, both as free liquid and hydrate. And finally, as the temperature increases from 100°C to 500°C, there is a progressive mass loss due to the evaporation of nitrogen compounds formed during complexation and their fragments which volatilize or decompose in this range of temperature. In this range of temperature, there is also formation of coke particles, so the final mass after the thermogravimetric analysis finishes is around 50wt% of the initial mass.

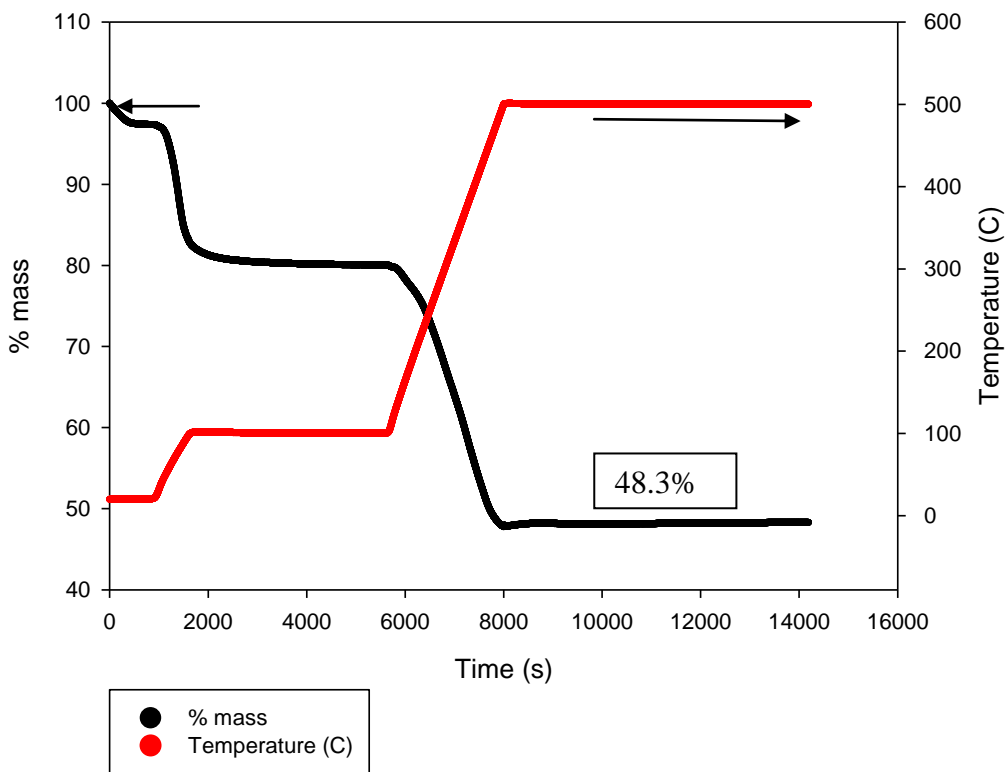


Figure 3-13 Mass loss of recovered copper chloride particles after reaction R72 by TGA in Ar

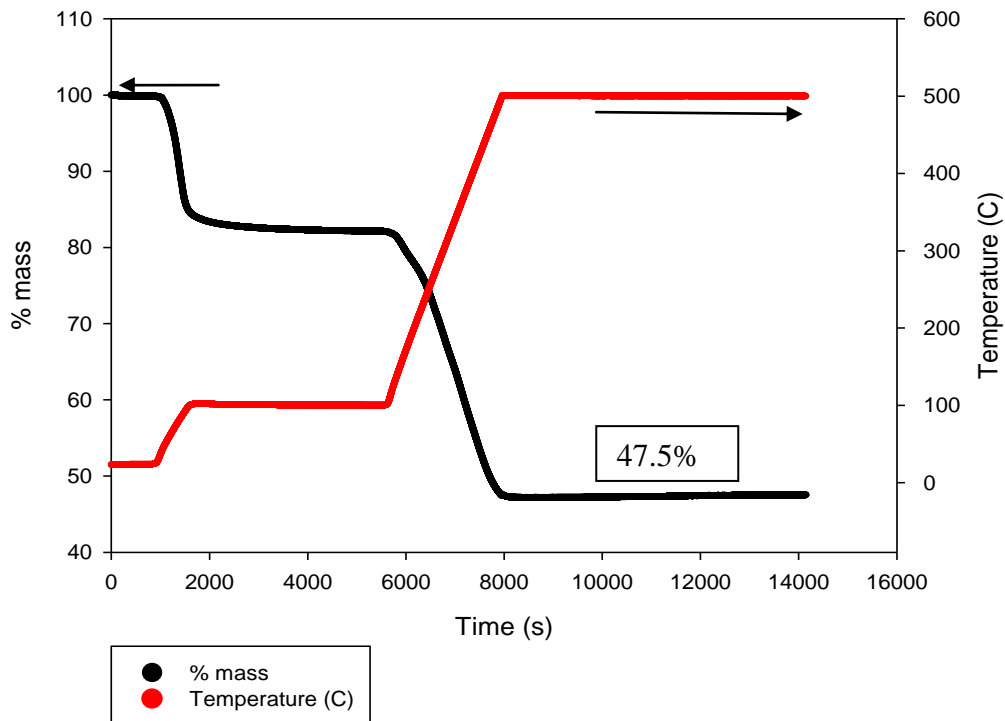


Figure 3-14 Mass loss of recovered copper chloride particles after reaction **R102** by TGA in Ar

3.3 Hydrotreatment

The hydrotreatment (HDT) experiments were conducted to assess the impact of removing large quantities of nitrogen compounds prior to HDT on the sulfur removal efficiency. Two different kinds of feed materials were used for the hydrotreatment experiments. The first kind of feed material was the untreated heavy gas oil; the second one was the denitrogenated oil obtained under the best nitrogen removal conditions. The sulfur removal performance was expected to be improved once the nitrogen species were removed from the oil.

Table 3-3 Nitrogen and sulfur content: hydrotreatment experiments

Feed Material/ Properties	Untreated coker heavy gas oil	Denitrogenated gas oil
N before HDT (ppmw)	5433	2278
S before HDT (wt %)	4.07	4.07
N after HDT (ppmw)	5277	2252
S after HDT (wt %)	3.83	3.39
% Sulfur removal	6.10 ± 0.58	16.78 ± 0.63

The reaction conditions chosen for the hydrotreatment experiments were not intended to achieve the maximum sulfur removal efficiency. The temperature and pressure values are in the range for the kind of feed material used in the experiments; however the reaction time is below the equivalent LHSV used in continuous industrial scale processes, where much higher sulfur removal would be targeted. The objective of the experiments was to confirm the impact of the nitrogen removal pretreatment on the sulfur removal performance. Improvement on sulfur removal efficiency after nitrogen reduction has been previously demonstrated in earlier studies^{13, 14, 20}

The results for the experiments are summarized in Table 3-3. These results showed that once the nitrogen content in the gas oil samples is reduced, the sulfur removal efficiency can be improved by more than two times at the same reaction conditions. This result is of great importance for industrial processes; once more, it is confirmed that the severity of the process conditions can be reduced (temperature, hydrogen pressure, etc) to get the same percentage of sulfur removal.

The nitrogen analysis of the products after hydrotreatment when using the denitrogenated oil as feed material shows that, the reduction on the nitrogen content achieved by the process is negligible. These results were expected since the reaction conditions are not severe enough to remove the non-basic nitrogen species present in the feed. These components would be mainly substituted carbazoles, which are the most difficult nitrogen species to remove by hydrotreatment^{64, 65}

3.4 Nitrogen compounds recovered from the copper complexes

The nitrogen compounds that were finally separated from the solid copper chloride particles after reaction/recovery and solvent evaporation are slightly sticky black solids. Due to their consistency, these solids had to be scratched from the evaporation flask once the solvent had been removed. The final product can be seen in Figure 3-15.



Figure 3-15 Nitrogen compounds obtained from copper complexation after solvent evaporation.

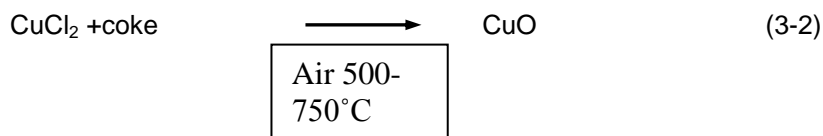
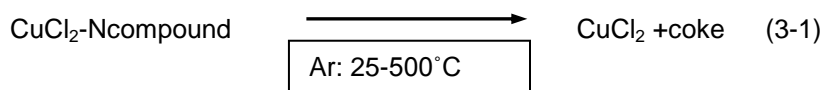
As previously mentioned in section 2.3.3; for the solids recovery, two different procedures were attempted. Procedure a) employed a mixture of dichloromethane and water as a liquid-liquid separation, this procedure was assumed to yield a more efficient separation. Procedure b) only employed dichloromethane as a solvent to wash the nitrogen compounds from the surfaces of the copper solid particles.

Thermogravimetric analyses of the recovered nitrogen compounds obtained by the two methods were conducted. These analyses served to determine how effective the separation process was, and also to analyze the behaviour of the mass of the nitrogen extracts with temperature. Figures 3-16 and 3-17 are the TGA data from two samples of nitrogen compound samples obtained using procedure b). In these experiments, the gas was switched from Argon to Air at 500°C. When the temperature reaches 500°C, most of the nitrogen compounds are volatilized or decomposed and some coke formation has taken place. The nitrogen extracts contain certain amounts of Cu and Cl in their structures. Previous studies on the thermal behaviour of various chloro complexes of

metals with 3-pyridinealdoxime⁶⁶ showed that the complexes are likely to decompose to the metal halide below 500°C and finally to the metal oxide between 500 and 660°C.

Xu-Wu et al.⁶⁷ studied the thermal behaviour of the copper (II) complex of 6-benzylaminopurine from 25 to 750°C. In this study they found that the complex experiences two successive courses of mass loss up to the final steady state (725°C). The mass loss is probably due to the rupture of the corresponding organic ligand. X-ray powder diffraction was used to determine that the final product in the process was CuO.

The behaviour of individual nitrogen complexes is different under the same thermal conditions. The great variety of nitrogen species produced in the complexation process make difficult to generate a general conclusion on the steps that the particles undergo during the heating process. In this study, switching the gas from Ar to air at the end of the analysis was intended to oxidize most of the remaining mass of sample to CuO and CuO₂. Equations 3-1 and 3-2 illustrate the main steps during the heating process.



Figures 3-16 and 3-17 show that the residue corresponds to circa 5% of the initial sample mass. The mass loss of the sample in air is in the range of 20-25% for the two figures. If the residue consists of only copper oxides, this mass loss is consistent with the loss of Cl in the molecules and replacement by O and O₂ due to oxidation.

Consequently, if we assume that all the copper in the sample is oxidized to copper (II) oxide (CuO), the amount of Cu present in the nitrogen extracts corresponds to 3.95% of the sample. This amount indicates that in the solids recovery step, significant quantities of copper are lost with the nitrogen compounds.

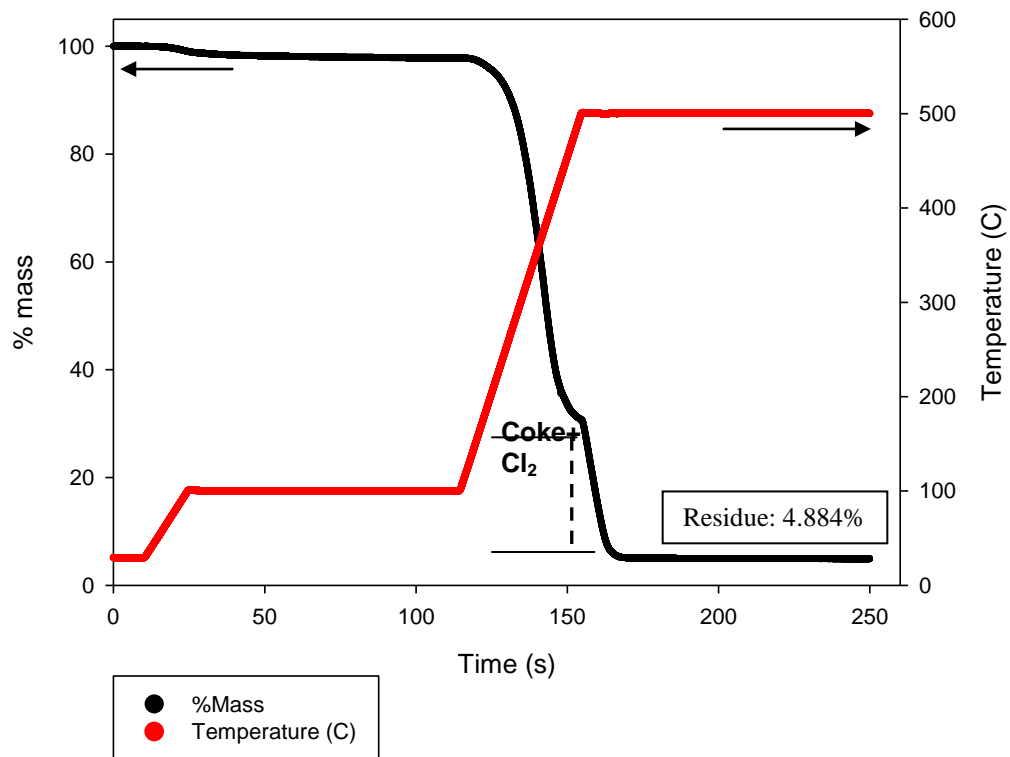


Figure 3-16 Mass loss of Nitrogen compounds obtained from copper complexation after solvent evaporation (R72) by TGA in N₂/Air

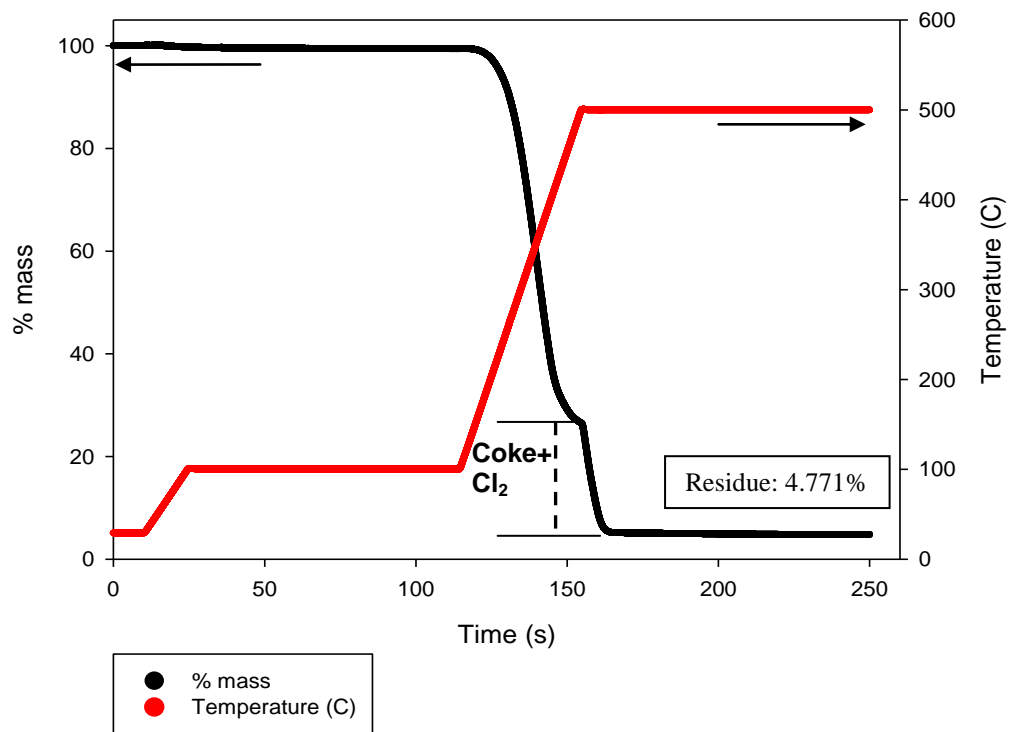


Figure 3-17 Mass loss of Nitrogen compounds obtained from copper complexation after solvent evaporation (R118) by TGA in N₂/Air

Figure 3-18 and 3-19 are the TGAs of samples of nitrogen complexes obtained by “procedure a” section 2.3.3. The results show that when “procedure a” is employed for the separation, the percentage of the initial mass obtained as final residue is significantly reduced. The two figures below show that around 1.5% of the initial mass remains after the analysis. If the same analysis carried out for Figures 3-16 and 3-17 is applied to the Figures below, it can be concluded that approximately 1.2% of copper remains with the nitrogen extracts. The analyses confirmed the initial idea that using methylene chloride plus water will offer a more efficient separation of the copper chloride from the nitrogen compounds.

The amount of coke formed during the heating process can be calculated by using the mass loss under the oxygen containing atmosphere. Assuming CuO of at the end of the process, the amount of Cu was calculated based on this value, the amount of Cl₂ is determined from the formula CuCl₂ and, by difference, the amount of coke can be calculated. For the nitrogen rich extracts, the mass of coke calculated correspond to 16 wt% for the samples obtained using the recovery “procedure a” and 20%wt for the ones using the recovery “procedure b”.

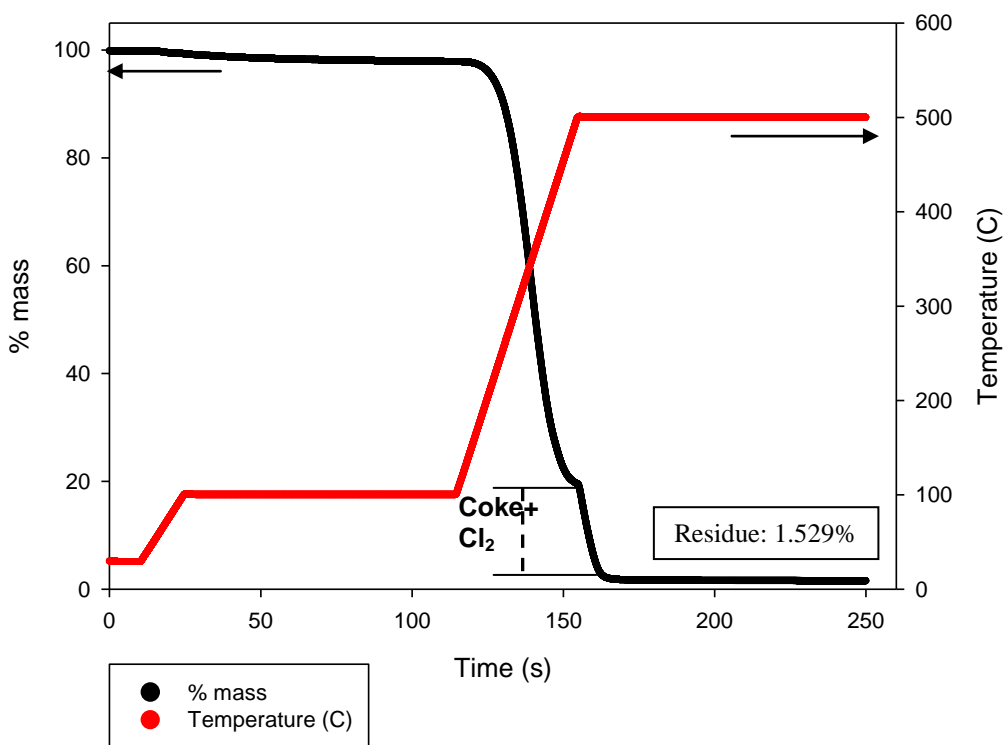


Figure 3-18 Mass loss of nitrogen compounds obtained from copper complexation after solvent evaporation (R113) by TGA in N₂/Air

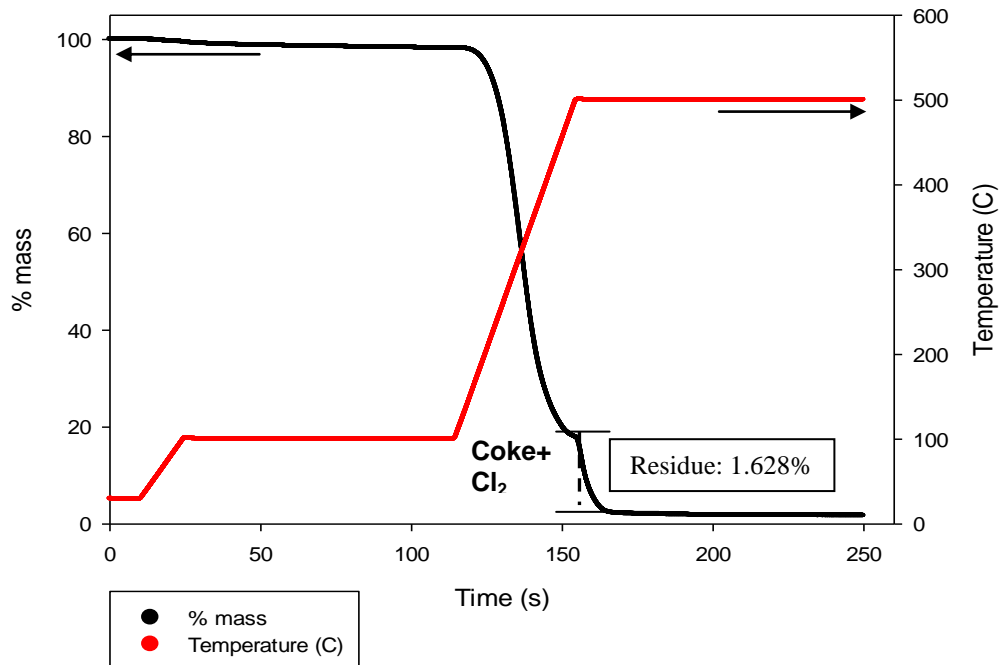


Figure 3-19 Mass loss of nitrogen compounds obtained from copper complexation after solvent evaporation (R117) by TGA in N₂/Air

3.5 Performance of the recovered copper chloride particles upon reuse

An experiment with the recovered copper chloride sample was carried out to confirm its performance upon reuse. The reaction conditions for this experiment were: 0.2 salt to oil weight ratio, 2h reaction duration and 8.65%wt of total water. The procedure for the reaction was identical to the procedure previously described in section 2.3

The nitrogen content of the denitrogenated oil sample showed nitrogen removal efficiency in the same range as the one obtained using the original copper chloride samples (58-60% at the best reaction conditions). Addition of free water for the reaction makes that variables such as particle size of the recovered salt particles have no influence on the efficiency of the removal process.

4. CONCLUSIONS AND RECOMMENDATIONS

The main conclusions of this study can be summarized as follows:

Extraction of nitrogen species by complexation with copper chloride is an efficient alternative for high nitrogen-containing feed oils. All the basic nitrogen can be eliminated from the samples and up to 60% of the initial total nitrogen can be removed.

Addition of liquid water for the reaction step is the novel invention in this study. Water dramatically improves both the rate of removal and the extent of removal. The presence of water partially dissolves some of the solid copper particles facilitating the contact with the nitrogen species in the oil at the interface.

The selected method was intended to target the basic nitrogen species, such as quinoline; but the results showed that up to 35% of the non-basic nitrogen species were also removed in the process.

The change on the sulfur content of the oil samples before and after reaction was negligible. This result shows high selectivity of the copper salt for nitrogen over sulfur compounds.

Decreasing the nitrogen content of the oil has a significant impact on hydrotreatment (HDT) of the same samples. The rate of removal of sulfur compounds on HDT experiments was increased by a factor of 2.5 using a standard commercial catalyst.

Therefore, selective removal of nitrogen compounds would allow less severe operation conditions.

Recovery of the copper chloride particles can be conducted by washing the solid reaction product with Methylene chloride and water, with subsequent solvent evaporation. The recovered particles exhibited the same performance in terms of nitrogen removal efficiency as the original copper (II) chloride salt.

The mass loss as a function of temperature of the nitrogen –rich extract demonstrated that vaporization and decomposition of the samples is occurring bellow 500°C. The thermogravimetric results indicate that the nitrogen rich extracts would not limit a gasifier operation.

Attempts to replicate this approach with heavier bitumen fractions were not successful, because the water-copper chloride-bitumen solution could not be separated. Consequently, the method is effective with gas oils and lighter distillates

The following items might be of interest for further study:

Analysis to determine the change in the composition of specific nitrogen compounds in the oil after the complexation step would be useful to assess the affinity of the copper salt for certain family of compounds.

The composition of the nitrogen rich extracts and the copper chloride particles after reaction is not completely understood, the use of other analytic techniques such as FTIR and powder diffraction could be useful to get a better understanding of their structures and composition.

REFERENCES

- (1) Drushel, H.; Sommers, A. Isolation and Identification of Nitrogen Compounds in Petroleum. *Anal. Chem.* **1966**, *38*, 19-8.
- (2) Jewell, D. M.; Snyder, R. E. Selective separation of "nonbasic" nitrogen compounds from petroleum by anion exchange of ferric chloride complexes. *Journal of Chromatography A* **1968**, *38*, 351-354.
- (3) Thompson, R.; Symon, T.; Wankat, C. Estimation of Pyrrole Nitrogen in Petroleum Distillates. *Anal. Chem.* **1952**, *24*, 1465-1467.
- (4) Hartung, G. K.; Jewell, D. M. Identification of nitriles in petroleum products : Complex formation as a method of isolation. *Anal. Chim. Acta* **1962**, *27*, 219-232.
- (5) Hartung, G.; Jewell, D. Carbazoles, Phenazines and Dibenzofuran in Petroleum Products, Methods of Isolation, Separation and Determination. *Anal. Chim. Acta* **1962**, *26*, 514-8.
- (6) Richter, F.; Caesar, P.; Meisel, S.; Offenhauer, R. Distribution of Nitrogen in Petroleum According to Basicity. *Industrial and Engineering Chemistry* **1952**, *44*, 2601-2605.
- (7) Shin, S. H.; Sakanishi, K.; Mochida, I.; Grudowski, D. A.; Shinn, J. H. Identification and reactivity of nitrogen molecular species in gas oils. *Energy Fuels* **2000**, *14*, 539-544.
- (8) Fu, C.; Schaffer, A. Effect of Nitrogen-Compounds on Cracking Catalysts. *Industrial & Engineering Chemistry Product Research and Development* **1985**, *24*, 68-75.
- (9) Narangerel, J.; Sugimoto, Y. Removal of nitrogen compounds before deep hydrotreatment of synthetic crude oils. *Journal of the Japan Petroleum Institute* **2008**, *51*, 165-173.
- (10) Sugimoto, Y.; Narangerel, J.; Ozawa, H. Deep Hydrotreatment of Middle Distillates Obtained by Pyrolysis of Oil Shale and Oil Sands Bitumen. *Journal of the Japan Petroleum Institute* **2010**, *53*, 101-104.
- (11) Loeffler, M.; Li, N. Role of Nitrogen-Containing and Sulfur-Containing-Compounds in the Aging of Liquid Fuels. *Fuel* **1985**, *64*, 1047-1053.
- (12) AnonymousDieselNet. <http://www.dieselnet.com/standards/> (accessed 08/23, 2011).
- (13) Choi, K.; Korai, Y.; Mochida, I.; Ryu, J.; Min, W. Impact of removal extent of nitrogen species in gas oil on its HDS performance: an efficient approach to its ultra deep desulfurization. *Applied Catalysis B: Environmental* **2004**, *50*, 9-16.
- (14) Laredo, G. C.; Altamirano, E.; De los Reyes, J. A. Inhibition effects of nitrogen compounds on the hydrodesulfurization of dibenzothiophene: Part 2. *Applied Catalysis A: General* **2003**, *243*, 207-214.
- (15) Yui, S.; Matsumoto, N.; Sasaki, Y. Athabasca oil sands produce quality FCC feeds. *Oil & Gas Journal* **1998**, *96*, 43-+.

- (16) Choi, H. W.; Dines, M. B. **1984**.
- (17) Almarri, M.; Ma, X.; Song, C. Selective Adsorption for Removal of Nitrogen Compounds from Liquid Hydrocarbon Streams over Carbon- and Alumina-Based Adsorbents. *Ind Eng Chem Res* **2009**, *48*, 951-960.
- (18) Charlesworth, J. Removal of Nitrogen-Compounds from Shale Oil by Adsorption on to Acid-Treated Shale Ash. *Fuel* **1986**, *65*, 1159-1163.
- (19) Min, W. S.; Choi, K. I.; Khang, S. Y.; Min, D. S.; Ryu, J. W.; Yoo, K. S.; Kim, J. H. **1999**.
- (20) Sano, Y.; Choi, K.; Korai, Y.; Mochida, I. Adsorptive removal of sulfur and nitrogen species from a straight run gas oil over activated carbons for its deep hydrodesulfurization. *Applied Catalysis B-Environmental* **2004**, *49*, 219-225.
- (21) Sano, Y.; Choi, K.; Korai, Y.; Mochida, I. Selection and further activation of activated carbons for removal of nitrogen species in gas oil as a pretreatment for its deep hydrodesulfurization. *Energy Fuels* **2004**, *18*, 644-651.
- (22) Choi, H.; Dines, M. Selective Removal of Nitrogen-Compounds from Shale Oil. *Fuel* **1985**, *64*, 4-8.
- (23) Kodera, Y.; Ukegawa, K.; Mito, Y.; Komoto, M.; Ishikawa, E.; Nakayama, T. Solvent-Extraction of Nitrogen-Compounds from Coal Liquids. *Fuel* **1991**, *70*, 765-769.
- (24) Qi, J.; Yan, Y.; Su, Y.; Qu, F.; Dai, Y. Extraction of nitrogen compounds from catalytically cracked diesel oil with a volatile carboxylic acid based on reversible chemical complexation. *Energy Fuels* **1998**, *12*, 788-791.
- (25) Serban, M.; Kocal, J. A. **2009**.
- (26) Xie, L.; Favre-Reguillon, A.; Pellet-Rostaing, S.; Wang, X.; Fu, X.; Estager, J.; Vrinat, M.; Lemaire, M. Selective Extraction and Identification of Neutral Nitrogen Compounds Contained in Straight-Run Diesel Feed Using Chloride Based Ionic Liquid. *Ind Eng Chem Res* **2008**, *47*, 8801-8807.
- (27) Xie, L.; Favre-Reguillon, A.; Wang, X.; Fu, X.; Pellet-Rostaing, S.; Toussaint, G.; Geantet, C.; Vrinat, M.; Lemaire, M. Selective extraction of neutral nitrogen compounds found in diesel feed by 1-butyl-3-methyl-imidazolium chloride. *Green Chem.* **2008**, *10*, 524-531.
- (28) Xie, L.; Favre-Reguillon, A.; Wang, X.; Fu, X.; Vrinat, M.; Lemaire, M. Selective Extraction of Neutral Nitrogen-Containing Compounds from Straight-Run Diesel Feed Using Polymer-Supported Ionic Liquid Moieties. *Ind Eng Chem Res* **2009**, *48*, 3973-3977.
- (29) da Conceicao, L.; de Almeida, C.; Egues, S.; Dallago, R.; Paroul, N.; do Nascimento, I.; de Souza, W.; Pergher, S. Preliminary study of the oxidation of nitrogen compounds of gas oil from Brazilian petroleum. *Energy Fuels* **2005**, *19*, 960-963.

- (30) Kim, S. J.; Chun, Y. J. Separation of Nitrogen Heterocyclic Compounds from Model Coal Tar Fraction by Solvent Extraction. *Separation Science & Technology* **2005**, *40*, 2095-2109.
- (31) Sugaya, K.; Nakayama, O.; Hinata, N.; Kamekura, K.; Ito, A.; Yamagiwa, K.; Ohkawa, A. Biodegradation of quinoline in crude oil. *Journal of Chemical Technology and Biotechnology* **2001**, *76*, 603-611.
- (32) Castorena, G.; Mugica, V.; Le Borgne, S.; Acuña, M. E.; Bustos-Jaimes, I.; Aburto, J. Carbazole biodegradation in gas oil/water biphasic media by a new isolated bacterium Burkholderia sp. strain IMP5GC. *J. Appl. Microbiol.* **2006**, *100*, 739-745.
- (33) Fu, C.; Schaffer, A. Effect of Nitrogen-Compounds on Cracking Catalysts. *Industrial & Engineering Chemistry Product Research and Development* **1985**, *24*, 68-75.
- (34) Nelson, N.; Levy, R. B. The organic chemistry of hydrodenitrogenation. *Journal of Catalysis* **1979**, *58*, 485-488.
- (35) Zeuthen, P.; Knudsen, K. G.; Whitehurst, D. D. Organic nitrogen compounds in gas oil blends, their hydrotreated products and the importance to hydrotreatment. *Catalysis Today* **2001**, *65*, 307-314.
- (36) Sumbogo Murti, S. D.; Yang, H.; Choi, K.; Korai, Y.; Mochida, I. Influences of nitrogen species on the hydrodesulfurization reactivity of a gas oil over sulfide catalysts of variable activity. *Applied Catalysis A: General* **2003**, *252*, 331-346.
- (37) Wiwel, P.; Knudsen, K.; Zeuthen, P.; Whitehurst, D. Assessing compositional changes of nitrogen compounds during hydrotreating of typical diesel range gas oils using a novel preconcentration technique coupled with gas chromatography and atomic emission detection. *Ind Eng Chem Res* **2000**, *39*, 533-540.
- (38) Gray, M. R. In *Fundamentals of oil sands upgrading*; 2009; .
- (39) Mohamed, F.; Taher, A. In *Fundamentals of Petroleum Refining*; Elsevier: 2010
- (40) Matar, S.; Hatch, L. F. In *Chemistry of Petrochemical Processes*; Butterworth-Hinemann: 2001
- (41) Gerloch, M.; Constable, E. C. In *Transition Metal chemistry: The Valence shell in d-chemistry block*; VCH Publishers: New York, 1994; .
- (42) Jones, C. J. In *d- and f-block chemistry*; J. Wiley: 2002; .
- (43) Sanchez-Delgado, R. A. In *Organometallic Modeling of the Hydrodesulfurization and Hydrodenitrogenation Reactions*; Kluwer Academic Publishers: Hingham, MA, USA, 2002
- (44) Heinrich, G.; Kasztelan, S. In Technip., Ed.; *Hydrotreating. Conversion Processes*. 2001
- (45) Geankoplis, C. J. In Prentice Hall Professional Technical Reference: 2003

- (46) Morris, D. In Wiley: *Principles of adsorption and adsorption processes*. Wiley-Interscience, 1984
- (47) Lesemann, M. F. M.; Setzer, C. Process for removal of nitrogen containing contaminants from gas oil feedstreams. US Patent 7160438 B2, January, **2004**.
- (48) Lee, S.; Ryu, J.; Min, W. SK hydrodesulfurization (HDS) pretreatment technology for ultralow sulfur diesel (ULSD) production. *Catalysis Surveys from Asia* **2003**, *7*, 271-279.
- (49) Wang, Y.; Li, R.; Liu, C. Removal of nitrogen compounds from lubricating base stocks with complexing of oxalic acid. *Fuel Process Technol* **2005**, *86*, 419-427.
- (50) Mochida, I.; Choi, K. H. In *Current progress in catalysts and catalysis for hydrotr.eating*. practical advances in petroleum processing; Springer New York: 2006
- (51) AnonymousThe chemogenesis web book. http://www.meta-synthesis.com/webbook/43_hsab/HSAB.html (accessed 03/25, 2011).
- (52) AnonymousBASF The Chemical company. <http://www.basionics.com/en/ionic-liquids/> (accessed 02/17, 2011).
- (53) Laus, G.; Bentivoglio, G.; Schottenberger, H. . Ionic Liquids: Current Developments, Potential And Drawbacks For Industrial Applications. *Lenzinger Berichte* **2005**, *71*.
- (54) AnonymousMerck Chemicals. http://www.merck-chemicals.com/ionic-liquids/c_g1ib.s1Lhu4AAAEWqOEFVhTI (accessed 02/15, 2011).
- (55) Zhang, S.; Zhang, Q.; Zhang, Z. Extractive desulfurization and denitrogenation of fuels using ionic liquids. *Ind Eng Chem Res* **2004**, *43*, 614-622.
- (56) Matsumoto, M.; Mikami, M.; Kondo, K. Separation of organic nitrogen compounds by supported liquid membranes based on ionic liquids. *Journal of the Japan Petroleum Institute* **2006**, *49*, 256-261.
- (57) Guth, E. D.; Diaz, A. F. Method for removing sulfur and Nitrogen in petroleum oils. US Patent 3847800, November, 1974.
- (58) Shiraishi, Y.; Tachibana, K.; Hirai, T.; Komasaawa, I. Desulfurization and denitrogenation process for light oils based on chemical oxidation followed by liquid-liquid extraction. *Ind Eng Chem Res* **2002**, *41*, 4362-4375.
- (59) Syncrude Canada Material Safety Data Sheet. **2006**.
- (60) Mireau, J. Patterns and Pathways of Hydrogenation of Asphaltene Model Compounds, University of Alberta, 2011.
- (61) Petroleum Analyzer Company Multitek Operation Manual. **2009**.
- (62) Richardson, S.; Gray, M. Enhancement of residue hydroprocessing catalysts by doping with alkali metals. *Energy Fuels* **1997**, *11*, 1119-1126.

- (63) mbraunusa mbraun. <http://www.mbraunusa.com/> (accessed 18/04, 2012).
- (64) Ferdous, D.; Dalai, A. K.; Adjaye, J. A series of NiMo/Al₂O₃ catalysts containing boron and phosphorus: Part II. Hydrodenitrogenation and hydrodesulfurization using heavy gas oil derived from Athabasca bitumen. *Applied Catalysis A: General* **2004**, *260*, 153-162.
- (65) Jokuty, P.; Gray, M. Resistant Nitrogen-Compounds in Hydrotreated Gas Oil from Athabasca Bitumen. *Energy Fuels* 1991, *5*, 791-795..
- (66) Allan, J.; McCloy, B. Thermal, Spectral and Magnetic Studies of the Chloro Complexes of Manganese, Cobalt, Nickel and Copper with 3-Pyridinealdoxime. *Thermochimica Acta* **1992**, *211*, 85-91.
- (67) Xu-Wu, Y.; Hang-Guo, Z.; Wu-Juan, S.; Xiao-Yan, W.; Sheng-Li, G. Thermochemistry of copper complex of 6-benzylaminopurine. *Journal of Thermal Analysis and Calorimetry* **2008**, *92*, 961-965.

APPENDIX A

Preliminary Experiments with copper chloride dihydrate and model mixtures

Copper chloride dihydrate, Quinoline, methylnaphthalene, and toluene were used for the preliminary experiments described below. The general procedure for these experiments was as follows: 20 or 30g of the sample were mixed with a known quantity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to get different $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to sample weight ratios; the mixture was placed in a magnetic stirrer for a determined period of time to let the complexation reaction proceed. The reaction was conducted at room temperature.

A.1 Model mixture 1: Quinoline with toluene as solvent

Quinoline is the simplest member of the quinoline series. It is a heterocyclic aromatic nitrogen compound characterized by a solid-ring structure containing benzene attached to pyridine at two adjacent carbon atoms. It is a yellowish oily liquid with a strong odour only slightly soluble in cold water but soluble in hot water and most organic solvents.

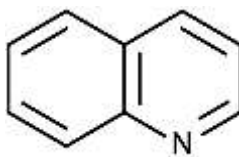


Figure A.1. Quinoline structure

Quinoline is classified as a basic compound given the unshared pair of electrons on the nitrogen atom. It is present in considerable amounts in petroleum and bitumen fractions. This is the main reason this compound was selected as a model compound for the preliminary experiments. Toluene and 1-methylnaphthalene were used as solvents for the preparation of the model mixtures.

A.1.1 Quinoline with Toluene as solvent

A solution of 2924 ppmwt of nitrogen was prepared using quinoline and toluene as solvent. 30g of the mixture were mixed with a determined amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in an erlenmeyer flask using a magnetic stirrer. The reaction times were 1.5 and 2h. After the reaction time elapsed, the product mixture was separated by filtration using a 0.8 μm pore size filter paper. The liquid phase was stored for future analysis. The solid particles with the extracted nitrogen compounds were also stored. The reaction conditions for each reaction are shown in Table A.1

Table A. 1. Reaction conditions for the” model mixture 1“ samples

Reaction #	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$:Mixture wt ratio	T (°C)	t (h)	Stirring velocity (rpm)
1	0.05	Room T	2	350
2	0.05	Room T	1.5	350
3	0.1	Room T	1.5	350
4	0.1	Room T	2	350

Qualitatively, the change on the color of the solid particles after the reaction suggests that at certain extent, the complexation reaction is in effect taking place between the copper salt and the quinoline present in the model mixture. The solid particles after filtration showed a change in their color from blue to dark green.

A.2 Model mixture 2: Quinoline with 1-methylnaphthalene as solvent

A second model mixture of 3000 ppmwt of nitrogen was prepared using quinoline and 1-methylnaphthalene as solvent. The same procedure describe in A.1 was followed for the experiments with “model mixture 2”.

Table A.2 Reaction conditions for the model mixture 2 samples.

Reaction #	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$:Mixture wt ratio	T (C)	t (h)	Stirring velocity (rpm)
5	0.1	Room T	1.5	350
6	0.1	Room T	2	350

A.3 Untreated Heavy Gas Oil

A modified experimental procedure was applied to an untreated heavy Gas Oil sample. The experimental conditions for the Gas oil samples are summarized in Table A.3. The reaction temperature for these samples was chosen to be 65°C. At this temperature, the viscosity of the sample is decreased enough to allow good mixing and mass transfer conditions.

Table A.3 Reaction conditions for untreated Gas Oil samples.

Reaction #	CuCl ₂ .2H ₂ O:Mixture wt ratio	T °C	t (h)	Stirring velocity (rpm)
7	0.100	65	2	350
8	0.125	65	2	350
9	0.100	65	2	350
10	0.150	65	2	350
11	0.050	65	2	350
12	0.080	65	2	350
13	0.180	65	2	350
14	0.200	65	2	350
15	0.250	65	2	350
16	0.100	65	2	350
17	0.100	65	2	350

The separation of the solid particles from the mixture by filtration at the same reaction temperature was ineffective due to the higher viscosity compared to the model mixtures. Simple decantation was then attempted; the reaction products were left for one hour at the same temperature to let the solid particles to precipitate. The later alternative was also ineffective when working with oil samples.

In order to make the filtration step easier, n-Hexane was added to the product mixture. Addition of hexane serves to decrease the viscosity of the sample, dissolves the non-nitrogen containing compounds from the solid particles, helps to minimize the gas oil losses in the process and increases the copper salt recovery in the process.

Vacuum filtration of the product mixture after n-Hexane addition was successfully completed. The solids containing the copper salt and the nitrogen complexes were recovered from the filter paper and stored for further treatment. The nitrogen compounds formed on the particles surface showed to be insoluble in solvents such as hexane or pentane. From the liquid phase, the solvent was separated from the mixture using a rotary evaporator and the mass of the recovered gas oil was recorded to finalize the mass balance.

An experiment to determine the required amount of hexane was conducted with one of the reactions product; the volume ratio of hexane was increased from 1:1 to 3:1 v/v, the solutions were mixed and they were let to separate for two days at room temperature. The 3:1 v/v mixture was found to give the highest amount of precipitates after decantation.

A.4 Copper chloride recovery

The recovery of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was attempted in two ways:

a) The recovered solid particles were dissolved in dichloromethane (DCM) and placed in a separation funnel; water was then added to the mixture, in this way, two phases were separated, the bottom phase containing the solvent and N-containing compounds and the top phase containing the aqueous solution of copper chloride. The water was evaporated from the aqueous phase under vacuum conditions. The challenge in this method is to dry the particles without removing the hydration water. The solvent was recovered from the bottom phase using a rotary evaporator. The mass nitrogen compounds formed in the process can be measured after solvent evaporation.

b) The solid particles were washed with a solvent capable of dissolving the N-containing compounds without dissolving the copper salt particles. Acetone and dichloromethane were tested as solvents and both were effective in dissolving the nitrogen complexes. The particles recovered when using dichloromethane showed to be qualitatively cleaner than when using acetone. Dichloromethane was selected as the solvent for these experiments. Finally, the solvent was separated from the liquid mixture using a rotary evaporator and the mass of the nitrogen compounds formed was measured and recorded.

A.5 Results and discussion

A.5.1 Model Mixture 1: Toluene+ Quinoline

At this point in the project, there was not nitrogen analyzer available to analyze the products from the preliminary experiments. A gas chromatography (GC) analysis was conducted on the liquid reaction products. The same analysis was conducted with the initial model mixture. Figures A.2 to A.5 show a comparison between the GC results for the model mixture and the liquid product of each reaction mention in Table A.1.

The efficiency of the nitrogen compounds removal can be qualitatively seen in the chromatograms.

The quinoline peak can be seen at around 4.76 min retention time. For the first three reactions, the intensity of the peak remains basically unchanged. The results from Figures A.2, A.3 and A.4 show that at these reaction conditions, negligible quantities of nitrogen can be removed from the model mixture.

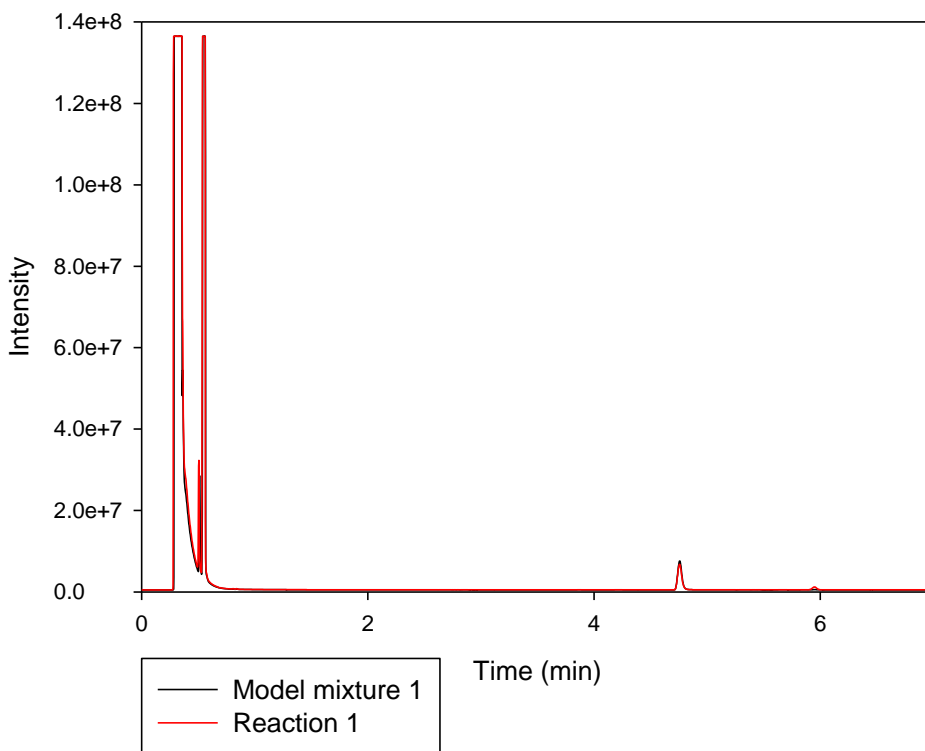


Figure A.2 Chromatogram of the products from reaction 1 compared to Model mixture 1.

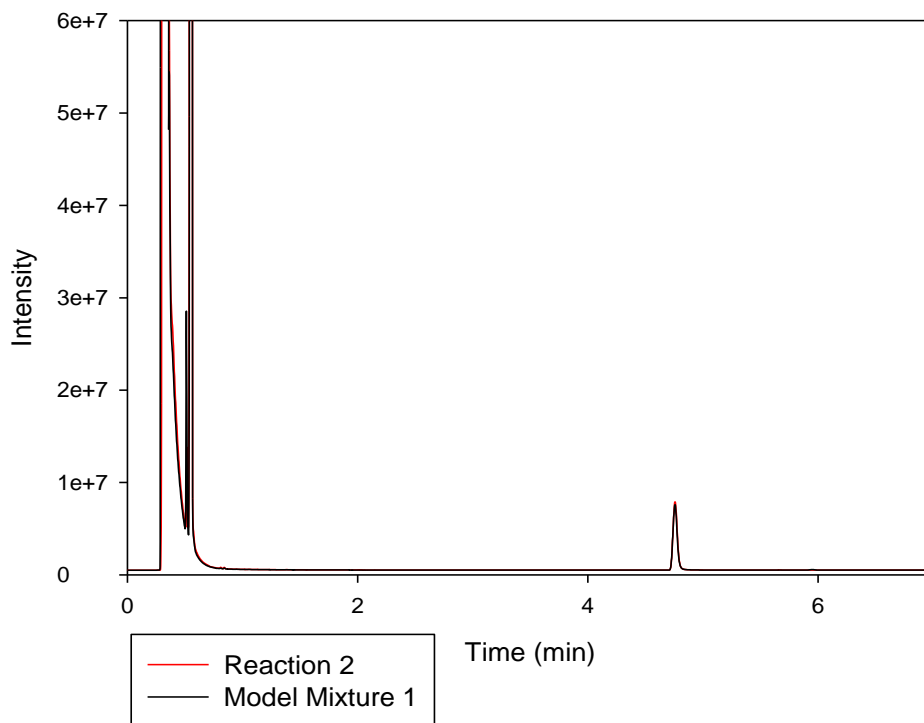


Figure A.3 Chromatogram of the products from reaction 2 compared to Model mixture 1.

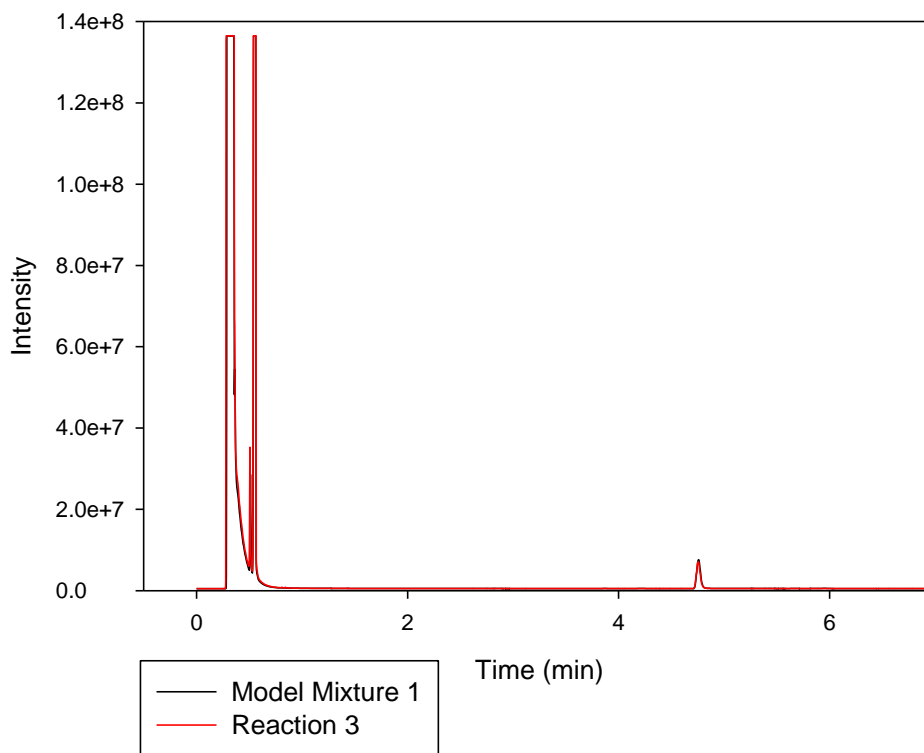


Figure A.4. Chromatogram of the products from reaction 3 compared to Model mixture 1.

The chromatogram shown in Figure A.5 is for the product of reaction 4. The graph shows that when the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to sample weight ratio increases from 0.05 to 0.1 and the reaction time is set to 2h, significant amount of quinoline removal can be achieved. This can be seen by the decreasing in the intensity of the quinoline peak.

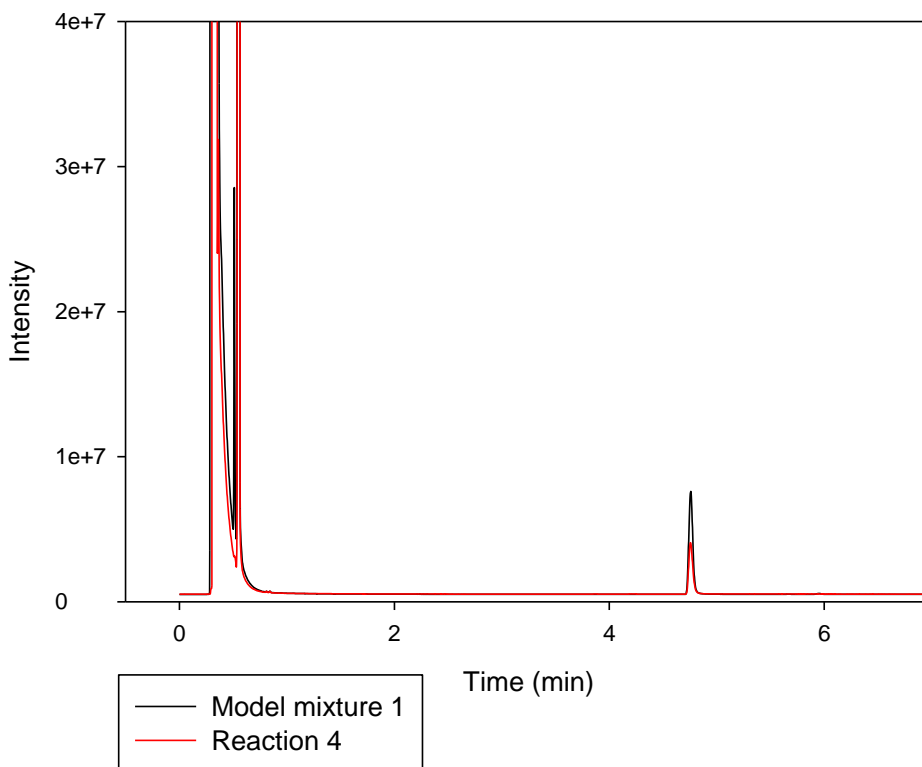


Figure A.5 Chromatogram of the products from reaction 4 compared to Model mixture 1.

A.5.2 Model Mixture 2: Methylnaphthalene+ Quinoline

GC- analysis for the reaction products was also conducted. The chromatograms of the products compared to the initial model mixture 2 are shown in Figures A.6 and A.7. The results show that there is an important decrease on the quinoline peak intensity in both reaction products. The reduction of the peak intensity indicates that the complexation reaction is taking place and more quinoline can be efficiently removed at these particular conditions.

The products of the reaction with the model mixture 2 showed two particular results: One is the change of color of the copper chloride particles after the reaction from blue to green/brown, the change is due to the quinoline complexes formed on the particles surface; the second one is that the initial color of the mixture also changed from yellowish

to greenish. This change can be attributed to that some of the N-containing compounds were soluble in the mixture, giving the particular color to the final solution.

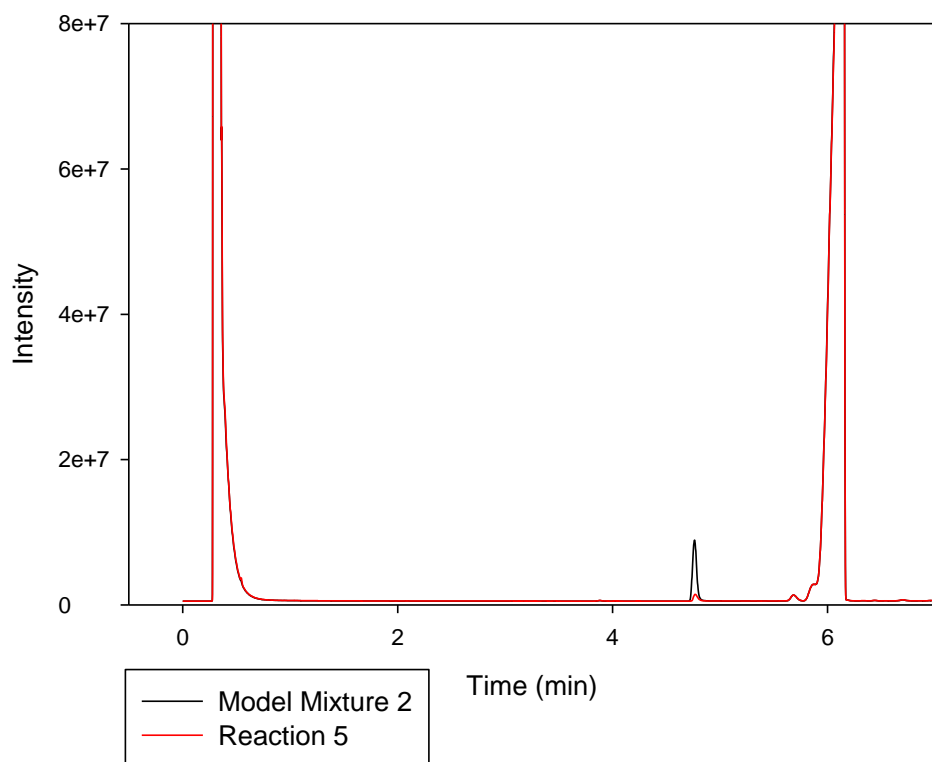


Figure A.6 Chromatogram of the products from reaction 5 compared to Model mixture 2.

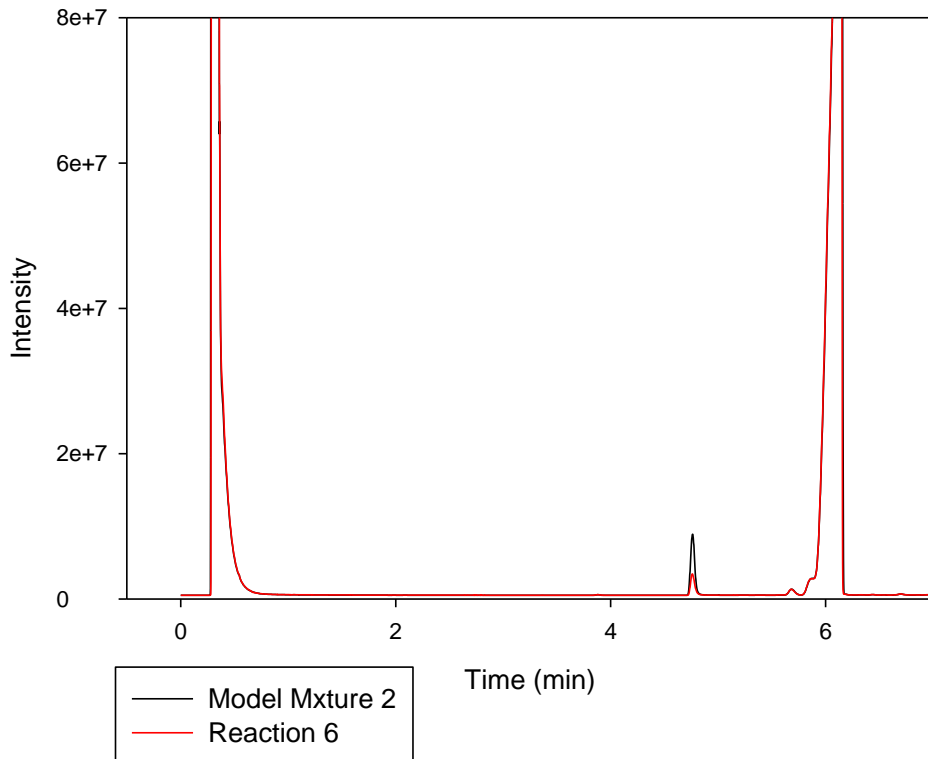


Figure A.7. Chromatogram of the products from reaction 6 compared to Model mixture 2.

A.5.3 Heavy gas oil

The nitrogen and sulfur content of the oil samples, before and after the complexation reaction could not be analyzed because of the lack of analytical capability in our laboratory at this point in the project. The gas oil samples were stored for future nitrogen and sulfur content analysis. The results allowed determining the nitrogen removal extent achieved by the process and also to determine the selectivity of the copper chloride for nitrogen compounds over sulfur compounds.

The only evidence that the complexation reaction was taking place between the nitrogen in the oil sample and the copper chloride particles is the change of the color of the particles after reaction. This change is proportional to the amount of nitrogen complexes formed during the process.

A.5.4 Athabasca Asphaltenes

An experiment using Athabasca asphaltenes and 1-methylnaphtalene as a solvent was attempted to assess the performance of the copper chloride salt when reacting with the

highest nitrogen containing materials, asphaltenes. The first limitation found in this experiment was the low solubility of the asphaltenes in the selected solvent. A saturated solution of the asphaltenes was then prepared, the nitrogen content of the final solution was below the range of heavy gas oil.

The complexation experiment was carried out using the same procedure described in section 2.5.5. The results of the experiment showed that the water-copper chloride-asphaltene solution could not be separated. Subsequently, the method is effective with gas oils and lighter distillates.

Based on the results of the preliminary experiments with the model mixtures and oil samples, the following observations can be summarized:

- Copper chloride salt reacts with the quinoline present in the mixture; however this interaction is improved by adequate mixing conditions, the amount of copper salt present in the mixture and the reaction duration.
- From the two experimental procedures for recovery of the copper chloride particles described in A.4, procedure a) is considered to be more effective in terms of salt recovery. The $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ particles recovered by this procedure have better physical appearance than the ones recovered by procedure b).
- The average oil losses achieved in the preliminary experiments are about 10% of the original sample. It is believed that these losses can be minimized by improving in handling and developing a better procedure.

APPENDIX B

Preliminary Experiments with Acid ionic liquid [BMIM]HSO₄

The use of ionic liquids as solvents for liquid-liquid extraction of nitrogen compounds from oil fractions was also considered as an alternative removal technique in this project. According to the literature results, 1-Butyl-3-methylimidazolium-Hydrogensulfate [BMIM]HSO₄ was found to be the most effective ionic liquid for extraction of nitrogen compounds from high nitrogen containing oil samples²⁵

Based on the previous results, [BMIM]HSO₄ was chosen as solvent to carry out some preliminary experiments with the untreated heavy gas oil samples. The chemical structure of 1-Butyl-3-methylimidazolium-Hydrogensulfate [BMIM]HSO₄ or C₈H₁₆N₂O₄S is shown in Figure B-1. [BMIM]HSO₄ contains an acidic anion and it is classified as acidic ionic liquid.

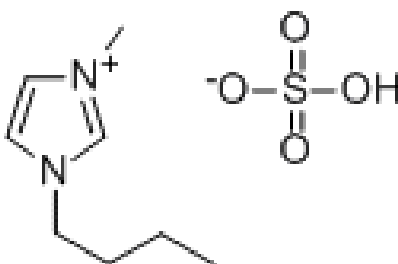


Figure B-1 Butyl-3-methylimidazolium-Hydrogensulfate [BMIM]HSO₄

The experimental procedure followed for the experiments described in this section can be summarized Figure B-2

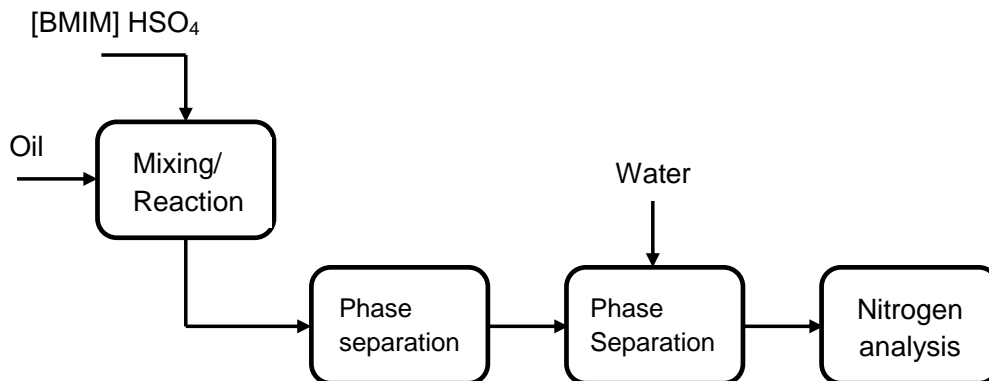


Figure B-2 Experimental procedure for ionic liquids

The experimental conditions for the extraction are shown in table B-1:

Table B-1 Experimental conditions for extraction with [BMIM]HSO₄

Variable	
Contact time (min)	30
[BMIM]HSO ₄ to Oil weight ratio	1
Temperature:	Room temperature
Agitation velocity (rpm)	350

The most interesting finding during this experimental work was that the separation of the phases after the mixing/reaction completion could not be carried out as described in the previous study²⁵. In this experimental set, once the contact time and mixing was elapsed, the mixture products stay as a semi-stable phase that could not be separated by simple decantation. The results obtained from the experiments do not agreed with the results reported in the literature for similar feed materials.

A complementary attempt to separate the ionic liquid from the oil in the product mixture was carried out. [BMIM]HSO₄ is a water soluble compound. Addition of water to the product mixture was then attempted. Water was intended to wash the ionic liquid with the absorbed nitrogen complexes from the oil and, in this way, facilitate the separation of the phases due to the difference in densities.

An experiment to determine how the addition of water would impact the phase separation was conducted. Samples of 1ml of the product mixture were taken and placed in 2ml vials, subsequently; water was added to the vials. The samples were manually agitated until the contents were well mixed and contacted. The vials were let to rest stable for about 2 days, this time was necessary to start seeing evidence of some extent of separation. Figure B-3 shows the results. From left to right, the amount of water added to the product mixture is increasing. It can be seen that separation of the phases is slowly enhanced when the amount of water increases. The long time necessary to achieve some separation of the ionic liquid and the oily phase is found to be impractical for any large scale application.



Figure B-3 Addition of water to 1ml of product mixture

Another experiment was conducted using larger amounts of product mixture. In this case, the agitation of the samples after water addition was carried out using a magnetic stirrer. Figure B-4 shows the results of this experiment. From left to right, the first flask contains only the ionic liquid with water; the second flask is the product mixture without any water added and, the other three flasks contain the product mixture with different amounts of water, the amount of water increases from left to right. The phase separation is not very clear in this experiment, in the last flask, separation of the ionic liquid plus water phase is more evident than in the others but there is also indication of an emulsion of oil- water development on the interphase.

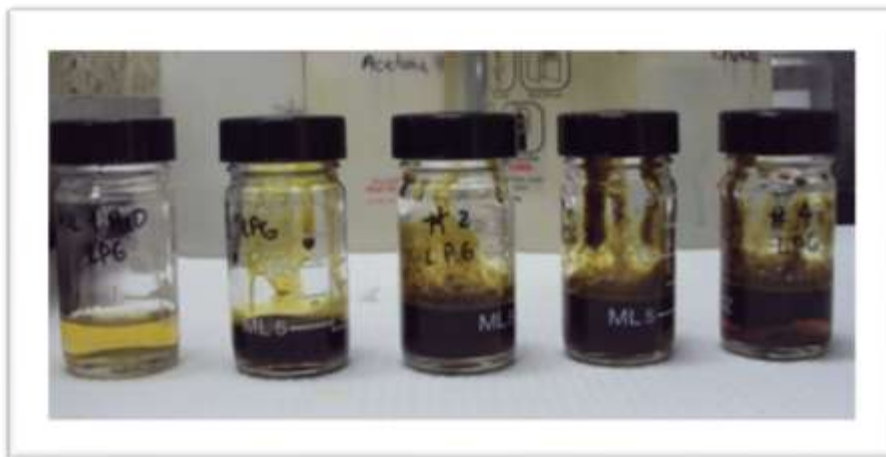


Figure B-4 Addition of water to 3.5ml of product mixture

Based on the results of the preliminary experiments with the ionic liquid and the oil samples, the following observations can be summarized:

- There is a big limitation concerning the phases separation, addition of water seems to be effective in dealing with this problem.
- Nitrogen and sulfur analysis of the oil samples from the oil phase after the phase separation would not give us any information on the efficiency of the process.
- According to the literature, the weight ratio of ionic liquid to oil required to get significant nitrogen removal in the process is of about 1. The failure to separate and further recover and reuse the ionic liquid, make this alternative costly for any practical application.
- The longer require to partially separate the product mixture, the failure to have a complete separation, the high cost and the amount of ionic liquid necessary for the experiments were the main reasons why this alternative was dismissed.

APPENDIX C

Report results: Canmet Energy Laboratories and Material Safety Data Sheet for the Gas oil Samples

C1. Nitrogen content Analysis for the first batch of samples

Sample No.	Sample ID	Analysis	Result	Units	Method
11-1438	Sample #22	Trace Nitrogen	4375	mg/kg	ASTM D4629
11-1439	Sample #23	Trace Nitrogen	4234	mg/kg	ASTM D4629
11-1440	Sample #24	Trace Nitrogen	4302	mg/kg	ASTM D4629
11-1441	Sample #25	Trace Nitrogen	4312	mg/kg	ASTM D4629
11-1442	Sample #26	Trace Nitrogen	4165	mg/kg	ASTM D4629
11-1443	Sample #27	Trace Nitrogen	3914	mg/kg	ASTM D4629
11-1444	Sample #28	Trace Nitrogen	3946	mg/kg	ASTM D4629
11-1445	Sample #29	Trace Nitrogen	2080	mg/kg	ASTM D4629
11-1446	Sample #30	Trace Nitrogen	2183	mg/kg	ASTM D4629
11-1447	Sample #31	Trace Nitrogen	2312	mg/kg	ASTM D4629
11-1448	Sample #32	Trace Nitrogen	2245	mg/kg	ASTM D4629
11-1449	Sample #33	Trace Nitrogen	2758	mg/kg	ASTM D4629
11-1450	Sample #34	Trace Nitrogen	2823	mg/kg	ASTM D4629
11-1451	Sample #35	Trace Nitrogen	2838	mg/kg	ASTM D4629
11-1452	Sample #36	Trace Nitrogen	2401	mg/kg	ASTM D4629
11-1453	Sample #37	Trace Nitrogen	3038	mg/kg	ASTM D4629
11-1454	Sample #38	Trace Nitrogen	3069	mg/kg	ASTM D4629
11-1455	Sample #39	Trace Nitrogen	3318	mg/kg	ASTM D4629
11-1456	Sample #40A	Trace Nitrogen	3537	mg/kg	ASTM D4629
11-1457	Sample #41B	Trace Nitrogen	3850	mg/kg	ASTM D4629

C2. Nitrogen content Analysis for the second batch of samples



Sample No.	Sample ID	Analysis	Result	Units	Method
11-1225	Sample #1	Trace Nitrogen	5448	mg/kg	ASTM D4629
11-1226	Sample #2	Trace Nitrogen	4555	mg/kg	ASTM D4629
11-1227	Sample #3	Trace Nitrogen	4409	mg/kg	ASTM D4629
11-1228	Sample #4	Trace Nitrogen	4337	mg/kg	ASTM D4629
11-1229	Sample #5	Trace Nitrogen	4276	mg/kg	ASTM D4629
11-1230	Sample #6	Trace Nitrogen	4650	mg/kg	ASTM D4629
11-1231	Sample #7	Trace Nitrogen	4626	mg/kg	ASTM D4629
11-1232	Sample #8	Trace Nitrogen	4324	mg/kg	ASTM D4629
11-1233	Sample #9	Trace Nitrogen	4267	mg/kg	ASTM D4629
11-1234	Sample #10	Trace Nitrogen	4628	mg/kg	ASTM D4629
11-1235	Sample #11	Trace Nitrogen	4735	mg/kg	ASTM D4629
11-1236	Sample #12	Trace Nitrogen	4238	mg/kg	ASTM D4629
11-1237	Sample #13	Trace Nitrogen	4282	mg/kg	ASTM D4629
11-1238	Sample #14	Trace Nitrogen	3622	mg/kg	ASTM D4629
11-1239	Sample #15	Trace Nitrogen	3540	mg/kg	ASTM D4629
11-1240	Sample #16	Trace Nitrogen	3374	mg/kg	ASTM D4629
11-1241	Sample #17	Trace Nitrogen	3313	mg/kg	ASTM D4629
11-1242	Sample #18	Trace Nitrogen	3253	mg/kg	ASTM D4629
11-1243	Sample #19	Trace Nitrogen	3074	mg/kg	ASTM D4629
11-1244	Sample #20	Trace Nitrogen	4741	mg/kg	ASTM D4629
11-1245	Sample #21	Trace Nitrogen	4873	mg/kg	ASTM D4629

C3. Basic Nitrogen content Analysis



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Sample No.	Sample ID	Analysis	Result	Units	Method
12-469	Sample 1 29-02-12	Total Base Number	6.7095	mg KOH/g	ASTM D2896
		Basic Nitrogen	1674.4	mg basic N/Kg	
12-470	Sample 2 29-02-12	Total Base Number	6.4525	mg KOH/g	ASTM D2896
		Basic Nitrogen	1610.2	mg basic N/Kg	
12-471	Sample 3 29-02-12	Total Base Number	0.00	mg KOH/g	ASTM D2896
		Basic Nitrogen	0.00	mg basic N/Kg	
12-472	Sample 4 29-02-12	Total Base Number	0.00	mg KOH/g	ASTM D2896
		Basic Nitrogen	0.00	mg basic N/Kg	

C4. Material safety data sheet for the coker heavy gas oil used in the experiments



MATERIAL SAFETY DATA SHEET

1. CHEMICAL PRODUCT & COMPANY IDENTIFICATION

PRODUCT: Coker Heavy Gas Oil

SAN 7681

MANUFACTURER:

Syncrude Canada Ltd.
P.O. Bag 4009
Fort McMurray, AB
Canada T9H 3L1
Emergency Telephone No. (780) 790-5094

SYNONYMS: Plant 8 Combined Gas Oil, Plant 8 Heavy Gas Oil, Coker Gas Oil
Gas Oil Hydrotreater Feed, Untreated Heavy Gas Oil
Syncrude Sample Tag # 081008, 081009, 082008, 082009, 083009, 151001,
152001

PRODUCT USE: Raw material for petroleum and petrochemical refining.

PREPARED BY: Nathalie Bérubé
(780) 790-4544

DATE OF PREPARATION/REVISION: March 7, 2006

2. COMPOSITION, INFORMATION ON INGREDIENTS

CAS #: 68478-17-1

A complex combination of hydrocarbons produced as the residual fraction from the distillation of the products from the fluid coking of bitumen. It consists of hydrocarbons having carbon numbers predominantly in the range of C13 to C60, boiling from approximately 230 °C (450 °F) to 620 °C (1150 °F).

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW:

A higher boiling hydrocarbon liquid. May cause irritation of the eyes, skin, gastrointestinal tract, and respiratory tract. Aspiration can lead to pulmonary edema and death. May affect many of the internal organs. Reproductive and developmental effects have occurred in experimental animals.

ROUTE OF ENTRY: Skin contact, skin absorption, eye contact, inhalation, ingestion.

EFFECTS OF ACUTE EXPOSURE:

EYES: May cause irritation with stinging and/or redness.

SKIN: May cause skin irritation. Results for skin sensitization were negative. Gas oils can defat the skin and can lead to oil acne, inflammation of the hair follicles, and development of warty growths under conditions of excessive exposure and poor personal hygiene.

INGESTION: May cause irritation of the mouth, throat and gastrointestinal tract. May cause vomiting which could lead to aspiration. Aspiration may result in lung damage, breathing difficulties, and potentially fatal chemical pneumonitis.

INHALATION: May irritate the mucous membranes of the respiratory tract. May cause headaches, nausea and mental confusion. Inhalation of gas oil vapours can lead to central nervous and respiratory system depression with possible loss of consciousness.

EFFECTS OF CHRONIC EXPOSURE:

EYES: Effects from chronic exposure were not reported in the literature.

SKIN: May cause dermatitis. May affect the heart, liver, bone marrow, kidneys, blood, liver, spleen, thymus and thyroid. Reproductive and developmental effects have been observed in experimental animals. Exposure may increase the risk of skin cancer.

INGESTION: Effects from chronic exposure were not reported in the literature.

INHALATION: Effects from chronic exposure were not reported in the literature.

4. FIRST AID MEASURES

INHALATION: Move victim to uncontaminated area. If breathing has stopped, trained personnel should begin artificial respiration, or, if the heart has stopped, cardiopulmonary resuscitation (CPR) immediately. Apply oxygen if available.

EYES: Immediately flush eyes with water; continue flushing for 15-25 minutes. Seek medical attention.

SKIN: Remove contaminated clothing. Wash affected area with soap and water. If irritation persists, seek medical attention.

INGESTION: DO NOT INDUCE VOMITING BECAUSE OF DANGER OF ASPIRATING LIQUID INTO LUNGS. If spontaneous vomiting occurs, monitor for breathing difficulty. Get immediate medical attention.

GENERAL: In all cases seek medical attention.

5. FIRE FIGHTING MEASURES

FLASH POINT, Pensky-Martens Closed Cup: 150 °C
FLAMMABLE LIMITS IN AIR: Not available
AUTO-IGNITION TEMPERATURE: 330 °C

FIRE & EXPLOSION HAZARDS:

Flammable near any source of ignition with vapour concentration within lower and upper explosion limits.

EXTINGUISHING MEDIA:

Class B fire extinguishers: Carbon Dioxide, dry powder, foam, polymer foam. Water fog can be used by trained fire prevention personnel.

FIRE FIGHTING PROCEDURES:

Evacuate all personnel from danger area. Exposed firefighters must wear full bunker gear, including a NIOSH approved positive pressure self-contained breathing apparatus with full face mask. Shut off sources of fuel and ignition. Stop flow of material, and contain spill. Cover with extinguishing media. Use water spray to cool fire-exposed containers, and as a protective screen. To avoid spreading fire, do not point solid water stream directly into burning material.

6. ACCIDENTAL RELEASE MEASURES

LEAK AND SPILL PROCEDURE:

Shut off all sources of ignition and evacuate area. Ventilate area of spill. Dike large spill with non-flammable material. Absorb on inert material and place in closed container for recycling or disposal. Personal Protective Equipment must be worn by clean-up crew.

7. HANDLING AND STORAGE

HANDLING PROCEDURES AND EQUIPMENT:

Avoid prolonged or repeated exposure to vapours. Avoid skin contact. Wash thoroughly after handling. Contact lens may absorb vapours and cause eye irritation.

STORAGE REQUIREMENTS:

Keep away from direct sunlight, heat, flame, or sources of spark. Do not store near oxidizing material. Provide adequate ventilation. Keep containers tightly closed and grounded.

8. EXPOSURE CONTROLS, PERSONAL PROTECTION

ENGINEERING CONTROLS:

Ventilate confined space before entry. Provide local exhaust where appropriate to minimize fugitive vapours or mists. Provide adequate general ventilation to dilute vapour concentrations within buildings.

PERSONAL PROTECTIVE EQUIPMENT:

Gloves: Acrylonitrile or neoprene
Respirator: NIOSH approved air purifying organic vapour at low concentrations (< 1000 ppm)
Eye: Monogoggles
Footwear: Rubber boots. Remove and change footwear if contaminated.
Clothing: Coveralls/apron as required.

EXPOSURE LIMITS:

8-hour OEL = 0.2 mg/m³ (benzene soluble aerosol)

9. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE: Dark brown, viscous liquid
ODOUR: Unpleasant hydrocarbon odour
PHYSICAL STATE: Liquid
pH: Not applicable
VAPOUR PRESSURE: 1.9 psia at 100 °C; < 1 psia (Reid Method)
VAPOUR DENSITY (Air = 1): Not available
FREEZING POINT: Not available
BOILING RANGE : 220 - 620 °C
SPECIFIC GRAVITY: 0.98 at 20 deg C
EVAPORATION RATE (n-Butyl Acetate = 1): 0.02
COEFFICIENT OF WATER/OIL DISTRIBUTION: Water insoluble, Oil miscible
ODOUR THRESHOLD: Not available

10. STABILITY AND REACTIVITY

STABILITY: Stable
CONDITIONS TO AVOID: Avoid exposure to sources of ignition
MATERIALS TO AVOID: Strong oxidizing materials. This material might soften or dissolve some plastics.
HAZARDOUS COMBUSTION PRODUCTS: Carbon dioxide, carbon monoxide, sulfur dioxide, uncombusted hydrocarbons, soot.

11. TOXICOLOGICAL INFORMATION

LD50: Studies reporting the LD50 were not located in the literature.
LC50: Studies reporting the LC50 were not located in the literature.

ACUTE:

Gastric haemorrhage and/or irritation, hypoactivity, ataxia, incontinence and hair loss were often observed during acute oral lethality studies involving rats. (Reference 1)

Rabbits used in acute dermal lethality studies often showed signs of irritation at the treatment area characterized by slight to severe erythema and oedema, followed by flaking/drying, crusting or thickening of the skin. (Reference 1)

Rats used in acute inhalation lethality studies often showed signs of marked inflammation of the lungs and respiratory tract. (Reference 1)

A heavy gas oil (boiling range = 415 - 525 °C; predominantly C21 - C37) was applied daily to the backs of rats for four weeks at doses of 25, 100 and 400 mg/kg/day. At the intermediate and high dose levels, a significant dose-related decrease in food intake and body weight gain was observed. Dose-related increases in blood urea nitrogen, cholesterol, and alkaline phosphatase were observed, along with, significant decreases in hemoglobin, hematocrit, red blood cell counts, and platelet counts. A significant decrease in mean corpuscular volume was observed at the intermediate and high dose levels. A significant increase in the relative liver and spleen weights (all three dose levels) and in the relative kidney weight (high dose level) was observed. Several organs were also affected by the treatment. Reduced cortical volume was detected at the intermediate dose and severe degenerative changes consisting of marked reduction in cortical and medullary volume was detected at the high dose in the thymus. In the thyroid, mild to moderate histological changes were observed at all dose levels. Males in the high dose group experienced moderate mantle zone atrophy with mild congestion and hyperplasia of the sinus areas in the spleen. Minimal to mild nuclear vesiculation and anisokaryosis was found in the liver at all dose levels. Epidermal hyperplasia was observed at all dose levels. (Reference 2)

SUBCHRONIC:

A "coker light gas oil", "heavy coker gas oil-1", "heavy coker gas oil-2", and "heavy coker gas oil-3" were four of several refinery streams applied to the skin of rats 5 day/wk for 13 weeks. The light oil and heavy oil-1 were applied at doses of 30, 125, 500 or 2000 mg/kg/day and the heavy oil-2 and heavy oil-3 were applied at doses of 8, 30 or 125 mg/kg/day. Signs of toxicity (combined for all the refinery streams tested) included increased mortality, decreased thymus weight, increased liver weight and aberrant serum chemistry and hematology. The LOEL (lowest-observed-effect-level) for increased liver weight was 30 mg/kg/day for the heavy oil-3 and the light oil. (Reference 3)

CHRONIC:

Studies reporting the effects from chronic exposure were not located in the literature.

CARCINOGENICITY:

The relative dermal carcinogenic potency (in comparison to 3-methylcholanthrene) of two coker gas oils were tested using mice. The mice were applied gas oil at 100 mg per application three times/wk. The relative carcinogenic potency was 0.10 and 0.39. (Reference 4)

Two gas oils (boiling range = 256 - 495 °C and 271 - 494 °C) were tested for their dermal carcinogenic potential in mice. The gas oils produced a tumor potency of 33 and 32% respectively. This corresponds to a 50% tumor response of 303 and 312 days respectively. (Reference 5)

Two fractions (boiling range = 288 - 371 °C and 371 - 577 °C) from two crude oils were applied (50 mg) to the skin of 50 mice twice per week for a minimum of 18 months. The tumor incidence rate was 17 and 3% for the first fraction and 82 and 87% for the second. The average latency period was 59 and 40 weeks and 50 and 34 weeks for the first and second fractions respectively. (Reference 6)

REPRODUCTIVE TOXICITY:

A "coker light gas oil", "heavy coker gas oil-1" and a "heavy coker gas oil-2" were three of several refinery streams applied to the skin of pregnant rats on days 0 to 19 gestation. The applied dose was 15, 60, or 250 mg/kg/day for the light oil, 8, 30, 125, or 250 mg/kg/day for the heavy oil-1, and 8, 30, or 125 mg/kg/day for the heavy oil-2. The LOEL (lowest-observed-effect-level) for increased incidence of resorption was 125 mg/kg/day (54.5 and 78.0% resorbed) for heavy oils-1 and 2. A LOEL was not found for the light oil. (Reference 3)

TERATOGENICITY:

A "heavy coker gas oil" (characteristics not reported) was tested at doses of 8, 30, 125, and 250 mg/kg/day (experimental design not reported). Foetal effects (not specified) were observed at 125 mg/kg/day while maternal effects (type not reported) were observed at 30 mg/kg/day. (Reference 1)

MUTAGENICITY:

Two high boiling petroleum distillates (371 - 577 °C) were tested using a modified Salmonella/microsome assay. Both distillates were modestly mutagenic. (Reference 7)

The fractions boiling between 288 and 371 °C and 371 and 577 °C from two crude oils were tested for their mutagenic potential using Salmonella typhimurium with and without S-9 activation. Both fractions from both crude oils were non-mutagenic. (Reference 8)

SYNERGISTIC EFFECTS:

Studies reporting potentially synergistic products were not located in the literature.

12. ECOLOGICAL INFORMATION

Not available.

13. DISPOSAL CONSIDERATIONS

WASTE DISPOSAL: Recover for reuse and recycling on plant site. Small quantities off-site can be burned in a chemical incinerator equipped with afterburner and scrubber. Comply with relevant legislation.

14. TRANSPORT INFORMATION:

CANADIAN TRANSPORTATION OF DANGEROUS GOODS:

Not regulated.

15. REGULATORY INFORMATION

WHMIS CLASS: D-1B; D-2A

This product has been classified in accordance with the hazard criteria of the CPR and the MSDS contains all the information required by the CPR.

All compounds in this product are listed in the Canada Domestic Substances List (DSL) and the United States Toxic Substances Control Act (TSCA) Chemical Substance Inventory (1985).

16. OTHER INFORMATION**REFERENCES:**

1. CONCAWE. Gas Oils (Diesel Fuels/Heating Oils). CONCAWE. Brussels. 1996.
2. Poon, R., I. Chu, D. C. Villeneuve and V. E. Valli. Short-Term Toxicity of Bitumen Upgrading Products in the Rat Following Repeated Dermal Exposure. *Fundamental and Applied Toxicology*. 23:237-250. 1994.
3. Feuston, M. H., L. K. Low, C. E. Hamilton and C. R. MacKerel. Correlation of Systemic and Developmental Toxicities with Chemical Component Classes of Refinery Streams. *Fund. Appl. Toxicol.* 22:622-630. 1994.
4. Bingham, E., R. P. Trossett and D. Warshawsky. Carcinogenic Potential of Petroleum Hydrocarbons A Critical Review of the Literature. *J. Environ. Pathol. Toxicol.* 3:483-563. 1980.
5. Dietz, W. A., W. H. King Jr., W. Priestley, Jr. and J. Rehner, Jr. Properties of High Boiling Petroleum Products: Carcinogenicity Studies. *Ind. Eng. Chem.* 44(8):1818-1827. 1952.
6. Lewis, S. C., R. W. King, S. T. Cragg and D. W. Hillman. Skin Carcinogenic Potential of Petroleum Hydrocarbons 2. Carcinogenesis of Crude Oil, Distillate Fractions and Chemical Class Subfractions. In: *The Toxicology of Petroleum Hydrocarbons*. Ed. H. N. MacFarland, C. E. Holdsworth, J. A. MacGregor, R. W. Call and M. L. Kane. American Petroleum Institute, Washington, DC. pp185-195. 1982.
7. Carver, J. H., J. A. MacGregor and R. W. King. Mutagenicity and Chemical Characterization of Two Petroleum Distillates. *J. Appl. Toxicol.* 4(4):163-169. 1984.
8. Cragg, S. T., C. C. Conaway and J. A. MacGregor. Lack of Concordance of the Salmonella/Microsome Assay with the Mouse Dermal Carcinogenesis Bioassay for Complex Petroleum Hydrocarbon Mixtures. *Fundam Appl Toxicol.* 5:382-390. 1985.

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